Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information For:

A Unified Set of Experimental Organometallic Data Used to Evaluate Modern Theoretical Methods

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Methods

Computational details

All calculations were carried out using the development version of the GAUSSIAN suite of programs[1] using the **Def2-TZVPP** basis set.[2] We used a very large grid of 199 radial and 590 angular points in all calculations to avoid known integration issues with modern functionals.[3,4] We tested the performance of 101 DFT functionals, which span all categories of functional types, namely: Local spin density approximation (LSDA), generalized gradient approximation (GGA), hybrid GGA methods (HGGA), meta-GGA methods (MGGA), hybrid meta GGA functionals (HMGGA), range separated HGGA methods (RS-HGGA) and double hybrid (DH) functionals. In addition, we included HF and MP2 as representatives of low cost wave function work for comparison. The methods used in the present benchmark study are summarized in **Table 2** in the main article.

Test Set Specific Details

To lower computational cost, the study proceeded in the following way.

(i) We first chose a subset of 23 complexes from the database (complexes A to F; see **Table 1** in the main article) and a subset of 27 DFT functionals (1 local functional, 5 additional functionals per category for GGA, HGGA, MGGA and HMGGA, 6 RS-HGGA functionals, and HF; see (**Table S1**)) in order to save computational cost for the full optimization of complexes. We chose these functionals based on popularity among computational chemists and also based on the use in our research group, which is admittedly arbitrary. To minimize expense, double hybrid functionals and MP2 methods are excluded at this stage. Note that reactants and products of the dissociation all underwent geometry optimization with each evaluated method. The mean signed error (MSE), mean unsigned error (MUE), root mean square deviation (RMSD) and maximum absolute deviation (MAXD) for each method was then evaluated with respect to the experimental bond dissociation energies.

(ii) A reference functional was then selected. We chose the 'best performing functional' from step (i) as reference functional. Single point energy calculations were then performed on the reference functional's optimized geometries using all other functionals/methods listed in **Table S1**. (Using "double-slash" notation, this is a "Reference functional/def2-TZVPP//Tested Functional/def2-TZVPP"calculation.) We then added the reference functional's thermal/vibrational correction to the tested functional's SCF energy, and used these thermally corrected values to calculate the new BDE. (Note that this has a long precedence; for example, the vibrational corrections from another functional and frozen geometries are used in the G3/99 test bed of enthalpies of formation.)[5] Validation of this method is shown in the results below.

(iii) Step (ii) was then repeated for all the functionals and methods listed in **Table 1** all the 30 complexes in the full database. The intrinsic assumption is that step (ii) demonstrated that frozen geometries from one method could be used to test the efficacy of other methods,

and thus we can avoid geometry optimizations with some methods. (This is critical for large scale testing of double hybrids.)

Table S1: DFT functionals and *ab initio* methods used in the evaluation of bond dissociation energies (BDEs). Note that we performed full optimization on the subset of 23 complexes chosen.

	DFT Functionals/*ab initio* methods
LSDA	SVWN
GGA	B97D, BLYP, MPWPW91, PBEPBE, PW91PW91,
HGGA	APF, APFD, B3LYP, BHandHLYP, PBE1PBE
MGGA	BB95, M06-L, MPWB95, THCTH, TPSSTPSS
HMGGA	BMK, M06, M06-2X, M06-HF, TPSSH
RS-HGGA	HSE2PBE, HSEH1PBE, LC-ωPBE, ωB97, ωB97X, ωB97XD,
***Ab initio* methods**	HF

(i) Bond Dissociation Enthalpies (BDEs) while optimizing geometries

We computed the BDEs of 23 complexes (subset of database) using the 27 functionals (subset of functionals) listed in **Table S1**.The mean signed error (MSE), mean unsigned error (MUE), root-mean square deviation (RMSD) and maximum absolute deviation (MAXD) of BDEs with respect to experimental values for various functionals and methods are given in **Table S2.** The computed bond dissociation enthalpies (BDEs) along with the experimental values for the 23 complexes are given in **Table S5**. Note that all these values are based on fully optimized results.

Table S2: The mean signed error (MSE), mean unsigned error (MUE), root-mean square deviation (RMSD) and maximum absolute deviation (MAXD) for 27 DFT functionals and HF method.

	MSE	MUE	RMSD	MAXD
		LSDA		
SVWN	18.3	18.3	18.9	26.0
		GGA		
B97D	2.6	2.9	3.5	7.7
BLYP	-8.6	8.6	9.0	14.9
MPWPW91	-2.5	2.9	3.4	6.8
PBEPBE	0.0	2.1	2.5	4.8
PW91PW91	0.6	2.0	2.5	5.4
		HGGA		
APF	-4.2	4.3	4.8	8.5
APFD	11.9	11.9	12.3	17.2
B3LYP	-8.9	8.9	9.4	16.1
BHandHLYP	-11.4	11.4	12.3	21.9
PBE1PBE	-2.7	2.9	3.5	6.8
		MGGA		
BB95	-2.0	2.6	3.1	6.6
M06-L	-0.4	1.9	2.2	4.4
MPWB95	0.7	2.2	2.7	4.6
THCTH	-8.1	8.1	8.5	13.6
TPSSTPSS	-2.1	2.6	3.1	5.9

		HMGGA		
BMK	-5.6	5.6	6.3	11.1
MO6	0.3	1.8	2.0	3.4
M06-2X	-2.6	3.7	4.9	10.6
M06-HF	-0.7	4.4	5.2	10.0
TPSSH	-3.2	3.3	3.9	6.8
		RGGA		
HSE2PBE	-2.8	3.0	3.6	7.2
HSEH1PBE	-2.7	2.9	3.4	7.0
LC-ωPBE	-3.0	3.1	3.7	6.4
ωB97	-2.5	3.0	3.8	8.1
ωB97X	-3.5	3.8	4.5	9.7
ωB97XD	-0.2	2.0	2.6	6.3
		Ab initio		
HF	-18.3	18.3	19.4	32.8

To get an overall picture of the performance of the functionals a graphical representation of MUE and RMSD is shown in **Figure S1**.

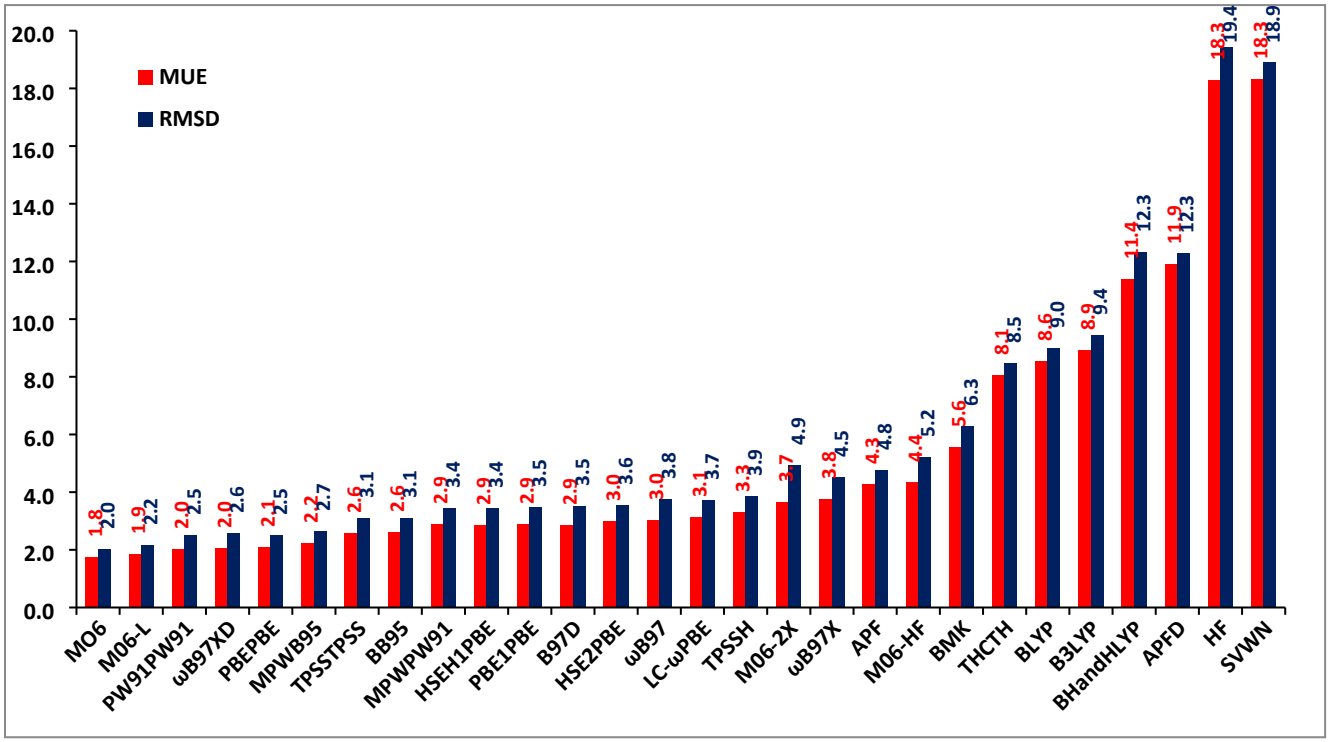

Figure S1: MUE and RMSD (kcal/mol) of BDEs for different functionals/methods (**Table S1**) in the ascending order of MUE values. The statistical parameters are based on BDEs calculated for 23 complexes after full optimization.

We found M06 is the best performing functional here and hence, chose this functional as the 'reference functional' for further calculations, i.e. we used M06 geometries.

(ii) BDEs from Frozen M06 geometries :

We then took the M06 optimized geometries as the reference structure and evaluated the approximate BDEs ($_{Frozen}BDE^{M06}$). The approximate BDEs utilize the SCF energy calculated with the evaluated functional plus the thermal correction obtained at the M06 level. (See **Table S6** for values) We then compared the $_{Frozen}BDE^{M06}$ with the optimized results for the same functionals. The MSE, MUE, RMSD and MAXD of $_{Frozen}BDE^{M06}$ are shown in **Table S3** along with the deviation from the optimized BDE results.

Table S3: The MSE, MUE, RMSD and MAXD values (kcal/mol) of $_{Frozen}BDE^{M06}$ values using M06 reference geometries and the deviation from the BDE (fully optimized) values.

		$_{Frozen}BDE^{M06}$				Deviation ($_{Frozen}BDE^{M06}$ – BDE)			
		MSE	MUE	RMSD	MAXD	MSE	MUE	RMSD	MAXD
LSDA	SVWN	16.9	16.9	17.6	25.9	-1.4	-1.4	-1.3	-0.1
GGA	B97D	2.7	3.0	3.7	8.1	0.2	0.2	0.2	0.4
	BLYP	-9.8	9.8	10.3	16.4	-1.3	1.3	1.3	1.4
	MPWPW91	-2.8	3.0	3.6	7.2	-0.3	0.1	0.2	0.4
	PBEPBE	-0.2	2.0	2.5	5.1	-0.2	-0.1	0.0	0.2
	PW91PW91	0.4	2.0	2.4	4.3	-0.2	-0.1	-0.1	-1.1
HGGA	APF	-4.4	4.4	4.9	8.6	-0.2	0.1	0.1	0.1
	APFD	11.6	11.6	12.0	17.3	-0.3	-0.3	-0.3	0.1
	B3LYP	-9.7	9.7	10.3	16.9	-0.8	0.8	0.8	0.8
	BHandHLYP	-12.7	12.7	13.8	23.1	-1.3	1.3	1.4	1.2
	PBE1PBE	-2.9	2.9	3.6	6.9	-0.2	0.0	0.1	0.1
MGGA	BB95	-2.1	2.7	3.2	6.6	-0.2	0.1	0.1	0.0
	M06-L	-0.6	1.9	2.2	4.5	-0.2	0.0	0.0	0.2
	MPWB95	0.6	2.2	2.6	4.6	-0.1	-0.1	-0.1	0.0
	THCTH	-8.9	8.9	9.2	13.9	-0.8	0.8	0.8	0.2
	TPSSTPSS	-2.3	2.6	3.2	6.1	-0.2	0.1	0.1	0.2
HMGGA	BMK	-5.5	5.5	6.2	10.8	0.1	-0.1	-0.1	-0.4
	MO6	0.3	1.8	2.0	3.4	0.0	0.0	0.0	0.0
	M06-2X	-3.1	4.1	5.4	11.1	-0.5	0.4	0.4	0.6
	M06-HF	-1.1	4.4	5.5	10.7	-0.3	0.0	0.2	0.7
	TPSSH	-3.3	3.4	3.9	6.9	-0.2	0.0	0.0	0.1
RS-GGA	HSE2PBE	-3.0	3.0	3.6	7.3	-0.1	0.0	0.0	0.1
	HSEH1PBE	-2.8	2.9	3.5	7.1	-0.2	0.0	0.1	0.1
	LC-ωPBE	-3.1	3.2	3.8	7.0	-0.1	0.1	0.1	0.5
	ωB97	-2.6	3.1	3.8	8.0	-0.1	0.1	0.1	-0.1
	ωB97X	-3.7	3.9	4.6	9.7	-0.2	0.2	0.1	0.0
	ωB97XD	-0.2	2.0	2.5	6.4	0.0	-0.1	-0.1	0.2
Ab initio	HF	-28.2	28.2	30.4	50.5	-10.0	10.0	10.9	17.7

It is obvious that the deviation of the approximate BDEs calculated on M06 geometries is very small for almost all functionals; with the exception HF, which can be attributed to HF's overall poor performance. For many functionals, the difference between the $_{Frozen}BDE^{M06}$ and BDEs by full optimization differs by a value as low as 0.0-0.2 kcal/mol. The functionals SVWN, BLYP, and BHandHLYP shows somewhat large deviation (close to 1.5 kcal/mol) followed by B3LYP and THCTH (0.8 kcal/mol). It can be concluded that our approach using M06 geometries and thermal corrections with the evaluated functionals SCF energy does not introduce significant error versus full optimization and vibrational analysis with the functional being tested.

Finally, to ensure this was not a fortuitous selection, we also evaluated the approximate BDEs ($_{Frozen}BDE^{\omega B97XD}$) with ωB97XD as the reference functional. The $_{Frozen}BDE^{\omega B97XD}$ values are given in **Table S7**. The MSE, MUE, RMSD and MAXD values of $_{Frozen}BDE^{\omega B97XD}$ and the deviation from the BDEs (fully optimized) are given in **Table S4**. This confirms that our "frozen geometry" approach is a valid one.

Table S4: The MSE, MUE, RMSD and MAXD values (kcal/mol) of $_{Frozen}BDE^{\omega B97XD}$ values using ωB97XD reference geometries and the deviation from the BDE (fully optimized) values.

		$_{Frozen}BDE^{\omega B97XD}$				Deviation ($_{Frozen}BDE^{\omega B97XD}$ – BDE)			
		MSE	MUE	RMSD	MAXD	MSE	MUE	RMSD	MAXD
LSDA	SVWN	16.4	16.4	17.1	24.8	-2.0	-2.0	-1.8	-1.3
GGA	B97D	2.5	2.9	3.5	7.4	-0.1	0.0	0.0	-0.3
	BLYP	-9.8	9.8	10.3	16.4	-1.2	1.2	1.3	1.5
	MPWPW91	-2.9	3.2	3.8	7.0	-0.5	0.3	0.3	0.1
	PBEPBE	-0.4	2.0	2.5	4.8	-0.5	-0.1	0.0	-0.1
	PW91PW91	0.2	1.9	2.4	4.9	-0.5	-0.1	-0.1	-0.4
HGGA	APF	-4.5	4.5	5.0	8.7	-0.3	0.2	0.2	0.2
	APFD	11.4	11.4	11.8	17.1	-0.5	-0.5	-0.5	-0.1
	B3LYP	-9.6	9.6	10.2	16.9	-0.7	0.7	0.7	0.8
	BHandHLYP	-12.4	12.4	13.5	23.1	-1.0	1.0	1.2	1.2
	PBE1PBE	-3.0	3.1	3.7	6.9	-0.3	0.2	0.2	0.2
MGGA	BB95	-2.4	2.8	3.4	6.6	-0.4	0.2	0.2	0.0
	M06-L	-0.7	2.0	2.3	5.0	-0.3	0.1	0.1	0.6
	MPWB95	0.3	2.1	2.5	4.2	-0.4	-0.1	-0.2	-0.5
	THCTH	-8.7	8.7	9.1	14.2	-0.6	0.6	0.6	0.5
	TPSSTPSS	-2.6	2.9	3.4	6.3	-0.4	0.3	0.3	0.4
HMGGA	BMK	-5.5	5.5	6.3	11.0	0.0	0.0	-0.1	-0.2
	MO6	0.0	1.8	2.0	3.8	-0.3	0.0	0.0	0.4
	M06-2X	-3.2	4.1	5.4	11.4	-0.5	0.4	0.5	0.8
	M06-HF	-1.2	4.5	5.5	10.8	-0.4	0.1	0.3	0.8
	TPSSH	-3.5	3.6	4.1	7.0	-0.3	0.3	0.2	0.2
RS-GGA	HSE2PBE	-3.0	3.1	3.7	7.4	-0.2	0.2	0.1	0.2
	HSEH1PBE	-2.9	3.1	3.6	7.2	-0.2	0.2	0.2	0.2
	LC-ωPBE	-3.2	3.3	3.9	6.7	-0.2	0.2	0.2	0.3
	ωB97	-2.6	3.1	3.8	8.2	-0.1	0.1	0.1	0.1
	ωB97X	-3.6	3.9	4.6	9.8	-0.1	0.1	0.1	0.2
	ωB97XD	-0.2	2.0	2.6	6.2	0.0	0.0	0.0	-0.1
Ab Initio	HF	-27.4	27.4	29.6	48.8	-9.1	9.1	10.1	16.0

(iii) Final pass to accumulate values in main paper.

We then used frozen BDE calculations for the complete list of 101 functionals and 2 ab inito methods listed in **Table 1** for all the 30 complexes in the database and the results are presented in the paper. It is to be noted that in the main paper, all the reported BDE values are computed at M06 optimized geometries. The computed BDEs are listed in **Table S8**.

(iv) Solvent corrections

Solvent effects were incorporated by using gas phase geometries and employing the SMD[6] solvation model for the twelve top performing functionals (those with MUEs below 2.5 kcal/mol) from gas-phase calculations. The list of solvents used in the experiments is listed in **Table S9**. The solvent corrected BDE values are given in **Table S10**.

References

(1) *Gaussian Development Version*, Revision H.08, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, G. Scalmani, B. Mennucci, V. Barone, G. A. Petersson, M. Caricato, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, X. Li, H. P. Hratchian, J. E. Peralta, A. F. Izmaylov, K. N. Kudin, J. J. Heyd, E. Brothers, V. Staroverov, G. Zheng, R. Kobayashi, J. Normand, J. L. Sonnenberg, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. C. Burant, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, W. Chen, M. W. Wong, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2006.

(2) Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.

(3) Wheeler, S. E.; Houk, K. N. *J. Chem. Theory Comput.* **2010**, *6*, 395.

(4) Johnson, E. R.; Becke, A. D.; Sherrill, C. D.; DiLabio, G. A. *J. Chem. Phys.* **2009**, *131*, 034111.

(5) Curtiss, L. a.; Raghavachari, K.; Redfern, P. C.; Pople, J. a. *J. Chem. Phys.* **2000**, *112*, 7374.

(6) Marenich, A. V; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B* **2009**, *113*, 6378.

Table S5: The calculated BDEs for 23 complexes in the subset of complexes from the database using functionals listed in **Table S1**

			LSDA	GGA					HGGA					MGGA				
Complex	Ligand L	Expt	SVWN	B97D	BLYP	MPW PW91	PBE PBE	PW91 PW91	APF	APFD	B3LYP	BH& HLYP	PBE1 PBE	BB95	M06-L	MPW B95	tHCTH	TPSS TPSS
$CpMn(CO)_2L$	η^2-2,3-dihydrofuran	28.4 ± 1.0	53.8	33.6	20.0	28.7	31.7	32.2	25.6	41.1	18.3	12.5	27.3	29.7	29.7	32.6	21.2	28.9
	chloropropane	16.0 ± 0.6	32.4	17.6	13.1	16.9	18.7	19.3	15.1	25.8	12.4	9.9	16.1	16.6	17.3	18.7	12.6	17.2
	η^2-cycloheptene	28.5 ± 0.8	50.9	31.7	16.2	25.1	28.2	28.7	22.2	40.6	14.9	9.6	23.9	26.4	27.2	29.6	17.2	25.6
	η^2-cyclooctene	34.9 ± 0.7	54.3	35.0	20.0	29.1	32.2	32.6	26.4	43.6	18.8	13.0	28.1	30.0	30.6	32.9	21.3	29.6
	η^2-furan	21.9 ± 1.0	41.5	24.5	12.8	20.3	22.8	23.3	17.6	32.6	11.6	8.1	19.0	20.5	20.7	23.1	13.7	20.7
	$S(n\text{-}Bu)_2$	36.0 ± 1.0	53.6	36.6	26.2	32.8	35.3	35.9	30.2	44.9	25.0	20.2	31.5	32.4	32.8	35.1	26.8	32.6
	tetrahydrothiophene	37.0	53.8	35.8	26.9	33.5	36.3	36.9	31.1	44.6	25.4	20.0	32.3	33.3	32.6	35.7	29.1	33.5
	THF	24.0 ± 3.0	35.0	23.4	16.0	18.2	20.1	21.0	17.8	31.0	16.6	16.0	18.9	18.1	22.5	19.9	14.1	19.3
	thiophene	19.5	39.8	22.9	16.6	22.4	24.3	24.9	20.2	30.3	15.7	11.8	21.3	21.6	20.5	23.7	17.5	22.3
	toluene	14.2 ± 0.8	35.1	19.9	6.0	12.6	15.4	15.9	10.2	28.9	5.5	3.4	11.7	13.4	15.2	16.3	6.4	13.0
	TES	27.4 ± 0.8	53.4	31.5	16.5	26.4	30.0	30.3	23.1	42.6	15.5	11.2	25.0	28.1	26.5	31.4	18.4	24.9
$BzCr(CO)_2L$	η^2-2,3-dihydrofuran	21.0 ± 1.0	44.9	26.3	12.8	20.6	23.5	24.1	18.7	34.5	12.2	9.7	20.5	22.1	23.5	25.1	13.3	21.1
	η^2-3-hexyne	22.8 ± 0.4	46.0	27.2	13.4	21.4	24.4	25.1	19.3	40.0	12.7	9.7	21.1	21.9	23.2	25.2	16.0	21.8
	η^2-benzene	11.5 ± 0.9	25.9	13.3	1.0	6.5	8.3	9.0	4.8	22.7	1.4	1.5	6.3	7.3	10.8	10.1	1.3	6.7
	TES	24.3 ± 1.2	45.4	25.1	11.6	19.2	22.8	23.1	17.7	38.7	11.5	9.6	19.8	21.3	21.8	24.7	12.2	18.5
	THF	21.4 ± 0.8	31.0	20.2	12.4	14.6	16.6	17.4	13.9	28.2	12.6	12.0	15.1	14.8	19.5	17.5	10.7	15.5
$Cr(CO)_5L$	η^2-benzene	11.4 ± 1.1	26.0	14.6	3.5	8.0	10.3	10.9	8.1	23.7	4.5	4.6	9.6	9.3	13.4	11.9	4.2	9.2
	η^2-3-hexyne	18.3 ± 0.7	39.6	20.6	8.7	16.6	19.5	20.1	16.3	31.6	9.7	8.4	18.3	17.6	20.2	20.8	9.8	17.8
$CpRe(CO)_2L$	heptane	13.7 ± 0.2	26.6	15.5	7.0	11.4	12.9	13.4	12.2	27.7	8.6	9.1	13.3	10.4	11.9	12.3	8.1	11.7
$(DMP)Mn(CO)_2L$	THF	22.1 ± 0.5	35.6	23.9	16.3	18.6	20.6	21.4	17.7	31.0	17.0	16.2	18.8	19.0	22.2	21.6	14.3	19.6
	η^2-benzene	14.9 ± 1.4	38.9	22.6	8.7	15.7	18.5	18.9	12.0	30.6	7.2	4.9	13.4	16.8	17.6	19.5	9.8	15.6
	bromohexane	21.1 ± 0.4	35.4	20.6	14.7	19.5	21.4	21.9	16.6	32.9	13.1	10.0	17.6	19.3	18.9	21.4	15.0	19.5
$TpRe(CO)_2L$	THF	23.9 ± 0.9	36.9	30.4	16.9	19.5	21.6	22.5	20.8	40.9	19.2	20.8	22.3	19.4	26.8	22.2	16.0	21.4
		MSE	18.3	2.6	-8.6	-2.5	0.0	0.6	-4.2	11.9	-8.9	-11.4	-2.7	-2.0	-0.4	0.7	-8.1	-2.1
		MUE	18.3	2.9	8.6	2.9	2.1	2.0	4.3	11.9	8.9	11.4	2.9	2.6	1.9	2.2	8.1	2.6
		RMSD	18.9	3.5	9.0	3.4	2.5	2.5	4.8	12.3	9.4	12.3	3.5	3.1	2.2	2.7	8.5	3.1
		MAXD	26.0	7.7	14.9	6.8	4.8	5.4	8.5	17.2	16.1	21.9	6.8	6.6	4.4	4.6	13.6	5.9

Complex	Ligand L	Expt	HMGGA					RGGA						Ab Initio
			BMK	M06-2X	M06-HF	M06	TPSSh	HSE2PBE	HSHE1PBE	LC-ωPBE	ωB97	ωB97X	ωB97XD	HF
$CpMn(CO)_2L$	η^2-2,3-dihydrofuran	28.4 ± 1.0	22.4	23.0	22.8	30.9	27.2	26.8	27.0	27.5	25.7	24.2	27.9	1.9
	chloropropane	16.0 ± 0.6	12.9	16.2	16.9	17.8	16.2	16.3	16.3	15.2	16.2	15.6	16.5	3.1
	η^2-cycloheptene	28.5 ± 0.8	19.5	21.2	21.6	27.7	24.0	23.5	23.7	24.1	22.8	21.3	26.2	1.2
	η^2-cyclooctene	34.9 ± 0.7	23.8	24.3	24.9	31.8	28.1	27.7	27.9	28.6	26.8	25.2	29.9	2.1
	η^2-furan	21.9 ± 1.0	15.0	17.0	18.9	22.1	19.2	18.8	18.9	18.9	17.4	16.4	19.7	1.7
	$S(n\text{-}Bu)_2$	36.0 ± 1.0	26.1	27.6	27.7	34.1	31.2	31.5	31.6	31.1	30.6	29.7	33.1	7.9
	tetrahydrothiophene	37.0	26.4	26.8	29.0	33.9	31.5	31.7	32.3	31.2	30.8	30.0	31.9	9.6
	THF	24.0 ± 3.0	18.8	23.3	25.6	22.5	18.8	19.5	19.4	19.1	22.0	21.1	23.0	9.1
	thiophene	19.5	16.2	17.2	18.4	22.1	21.2	21.3	21.3	20.7	19.9	19.3	21.0	3.0
	toluene	14.2 ± 0.8	8.4	14.1	15.9	15.8	11.7	11.7	11.8	10.5	11.8	10.5	15.0	0.3
	TES	27.4 ± 0.8	18.4	19.5	19.2	27.6	23.4	24.4	24.7	25.9	25.1	22.8	27.5	2.3
$BzCr(CO)_2L$	η^2-2,3-dihydrofuran	21.0 ± 1.0	17.8	20.5	21.7	24.3	19.9	20.1	20.3	19.1	17.8	17.3	21.7	1.0
	η^2-3-hexyne	22.8 ± 0.4	19.0	21.5	25.3	24.1	20.5	20.7	20.9	20.5	18.9	18.5	24.1	8.0
	η^2-benzene	11.5 ± 0.9	5.5	10.6	13.6	10.4	5.9	6.4	6.5	5.1	8.2	7.1	10.3	-0.1
	TES	24.3 ± 1.2	16.2	18.6	20.5	23.0	17.6	19.2	19.6	19.4	19.0	17.9	23.3	1.8
	THF	21.4 ± 0.8	15.1	19.9	21.9	18.9	14.9	15.6	15.5	15.2	17.9	17.7	19.6	7.3
$Cr(CO)_5L$	η^2-benzene	11.4 ± 1.1	9.3	14.1	17.4	13.1	8.9	9.6	9.8	9.4	11.9	10.7	13.3	1.1
	η^2-3-hexyne	18.3 ± 0.7	17.8	20.4	25.1	20.8	17.2	17.9	18.1	17.9	18.2	17.3	20.5	1.2
$CpRe(CO)_2L$	heptane	13.7 ± 0.2	10.9	13.8	18.2	13.6	11.9	13.3	13.3	13.9	14.2	13.7	16.4	3.0
$(DMP)Mn(CO)_2L$	THF	22.1 ± 0.5	18.7	23.6	25.7	22.2	18.9	19.4	19.3	19.0	22.1	21.1	23.3	9.6
	η^2-benzene	14.9 ± 1.4	10.4	14.9	17.3	17.3	13.8	13.4	13.5	12.9	14.1	12.6	16.4	1.3
	bromohexane	21.1 ± 0.4	14.2	16.5	17.2	19.8	18.0	17.7	17.7	16.8	17.0	16.4	17.9	3.2
$TpRe(CO)_2L$	THF	23.9 ± 0.9	23.3	29.2	32.2	27.3	21.6	22.9	22.8	23.4	28.4	26.8	30.2	13.8
		MSE	-5.6	-2.6	-0.7	0.3	-3.2	-2.8	-2.7	-3.0	-2.5	-3.5	-0.2	-18.3
		MUE	5.6	3.7	4.4	1.8	3.3	3.0	2.9	3.1	3.0	3.8	2.0	18.3
		RMSD	6.3	4.9	5.2	2.0	3.9	3.6	3.4	3.7	3.8	4.5	2.6	19.4
		MAXD	11.1	10.6	10.0	3.4	6.8	7.2	7.0	6.4	8.1	9.7	6.3	32.8

Table S6: Approximate BDEs ($_{Frozen}BDE^{M06}$) calculated on M06 geometries using DFT functionals/methods listed in **Table S1** for the subset of complexes.

			LSDA	GGA					HGGA					MGGA				
Complex	Ligand L	Expt.	SVWN	B97D	BLYP	MPW PW91	PBE PBE	PW91 PW91	APF	APFD	B3LYP	BH& HLYP	PBE1 PBE	BB95	M06-L	MPW B95	tHCTH	TPSS TPSS
$CpMn(CO)_2L$	η^2-2,3-dihydrofuran	28.4 ± 1.0	53.4	33.8	18.5	28.7	31.8	32.2	25.6	40.9	17.6	11.1	27.2	29.7	29.6	32.7	20.9	28.9
	chloropropane	16.0 ± 0.6	31.4	17.7	12.3	16.7	18.5	19.1	14.9	25.9	12.0	9.6	16.0	16.5	17.2	18.7	12.2	17.0
	η^2-cycloheptene	28.5 ± 0.8	50.3	32.0	14.8	25.0	28.3	28.7	22.1	40.5	14.1	7.9	23.9	26.5	26.9	29.6	16.9	25.6
	η^2-cyclooctene	34.9 ± 0.7	54.0	35.3	18.5	29.0	32.2	32.6	26.3	43.7	18.0	11.8	28.0	30.1	30.4	33.0	21.0	29.5
	η^2-furan	21.9 ± 1.0	41.0	24.6	11.6	20.1	22.8	23.2	17.6	32.4	10.9	6.0	19.0	20.6	20.5	23.2	13.4	20.6
	$S(n\text{-}Bu)_2$	36.0 ± 1.0	53.0	36.7	25.2	32.8	35.3	35.9	30.0	44.9	24.5	19.8	31.4	32.5	32.8	35.2	26.6	32.5
	tetrahydrothiophene	37.0	53.5	35.9	26.7	34.1	36.4	36.9	31.0	43.0	25.6	20.4	32.2	33.4	32.7	35.9	28.3	33.5
	THF	24.0 ± 3.0	33.5	23.0	14.7	17.5	19.5	20.3	17.5	31.2	15.9	15.8	18.7	17.4	22.1	19.9	13.1	18.7
	thiophene	19.5	37.7	22.9	14.9	21.0	23.0	23.6	18.9	30.3	14.5	11.1	20.1	20.2	20.2	22.5	15.9	21.0
	toluene	14.2 ± 0.8	32.0	19.5	4.0	11.6	14.4	14.9	9.4	29.0	3.7	0.3	10.9	12.6	14.8	15.5	5.0	12.1
	TES	27.4 ± 0.8	53.3	32.1	14.9	26.8	30.5	30.7	23.5	42.9	13.9	5.8	25.4	28.5	26.4	31.7	18.1	25.4
$BzCr(CO)_2L$	η^2-2,3-dihydrofuran	21.0 ± 1.0	43.7	26.6	11.3	20.4	23.5	24.0	18.7	34.5	11.4	8.5	20.5	22.0	23.1	25.1	12.5	21.0
	η^2-3-hexyne	22.8 ± 0.4	43.7	27.2	11.6	20.6	23.8	24.4	18.9	40.1	11.7	9.0	20.9	21.7	23.0	25.0	13.4	21.3
	η^2-benzene	11.5 ± 0.9	21.6	13.6	0.0	5.5	7.9	8.5	4.8	22.5	0.6	-0.1	6.2	6.9	10.6	9.5	0.4	6.4
	TES	24.3 ± 1.2	43.6	25.5	8.8	19.3	22.8	23.2	17.9	38.7	9.4	6.3	20.0	21.3	21.5	24.6	10.6	18.8
	THF	21.4 ± 0.8	30.0	20.5	11.2	14.2	16.3	17.1	13.5	28.1	11.8	11.2	14.8	14.8	19.4	17.5	9.6	15.3
$Cr(CO)_5L$	η^2-benzene	11.4 ± 1.1	23.3	14.8	2.5	8.0	10.3	10.9	8.1	23.6	3.9	3.9	9.6	9.3	13.3	11.9	3.3	9.1
	η^2-3-hexyne	18.3 ± 0.7	38.5	20.8	7.3	16.0	19.2	19.8	16.0	31.6	8.9	7.8	18.1	17.5	19.8	20.8	8.7	17.4
$CpRe(CO)_2L$	heptane	13.7 ± 0.2	24.1	15.2	5.8	10.6	12.2	12.8	11.6	25.9	7.9	8.7	12.8	10.0	11.7	11.9	7.2	11.1
$(DMP)Mn(CO)_2L$	THF	22.1 ± 0.5	34.8	24.2	15.9	18.7	20.8	21.6	17.7	31.3	16.2	15.0	18.9	18.6	22.2	21.2	14.2	19.7
	η^2-benzene	14.9 ± 1.4	36.1	23.0	8.0	15.5	18.2	18.7	12.1	30.9	6.6	2.3	13.5	16.8	17.4	19.5	9.4	15.6
	bromohexane	21.1 ± 0.4	34.6	20.5	13.4	19.0	21.0	21.5	16.4	28.5	12.5	9.1	17.4	18.9	18.8	21.1	14.3	19.1
$TpRe(CO)_2L$	THF	23.9 ± 0.9	36.0	30.9	16.3	19.3	21.5	22.5	20.7	40.6	18.8	20.6	22.2	19.5	26.8	22.3	15.6	21.2
		MSE	16.9	2.7	-9.8	-2.8	-0.2	0.4	-4.4	11.6	-9.7	-12.7	-2.9	-2.1	-0.6	0.6	-8.9	-2.3
		MUE	16.9	3.0	9.8	3.0	2.0	2.0	4.4	11.6	9.7	12.7	2.9	2.7	1.9	2.2	8.9	2.6
		RMSD	17.6	3.7	10.3	3.6	2.5	2.4	4.9	12.0	10.3	13.8	3.6	3.2	2.2	2.6	9.2	3.2
		MAXD	25.9	8.1	16.4	7.2	5.1	4.3	8.6	17.3	16.9	23.1	6.9	6.6	4.5	4.6	13.9	6.1

Complex	Ligand L	Expt.	HMGGA					RS-HGGA						Ab Initio
			BMK	M06-2X	M06-HF	M06	TPSSh	HSE2PBE	HSHE1PBE	LC-ωPBE	ωB97	ωB97X	ωB97XD	HF
$CpMn(CO)_2L$	η^2-2,3-dihydrofuran	28.4 ± 1.0	22.9	22.3	22.0	30.9	27.2	26.8	27.0	27.4	25.7	24.1	28.0	-13.6
	chloropropane	16.0 ± 0.6	13.5	15.8	17.2	17.8	16.1	16.2	16.2	15.1	16.0	15.5	16.6	-1.6
	η^2-cycloheptene	28.5 ± 0.8	20.2	20.4	20.9	27.7	24.0	23.5	23.7	24.1	22.9	21.3	26.4	-16.9
	η^2-cyclooctene	34.9 ± 0.7	24.1	23.8	24.2	31.8	28.0	27.6	27.8	28.5	26.9	25.2	30.1	-13.0
	η^2-furan	21.9 ± 1.0	14.9	15.4	16.5	22.1	19.2	18.7	18.9	18.9	17.4	16.3	19.7	-13.8
	$S(n\text{-}Bu)_2$	36.0 ± 1.0	26.6	27.1	28.3	34.1	31.1	31.4	31.5	30.9	30.4	29.5	33.0	1.7
	tetrahydrothiophene	37.0	27.1	26.5	27.2	33.9	32.0	32.2	32.3	31.6	30.8	30.0	32.6	2.1
	THF	24.0 ± 3.0	18.9	23.7	25.8	22.5	18.3	19.2	19.2	19.0	22.1	21.1	23.1	6.9
	thiophene	19.5	16.5	16.5	18.4	22.1	19.9	20.1	20.2	20.0	19.7	19.0	20.9	-3.0
	toluene	14.2 ± 0.8	8.1	12.0	14.3	15.8	10.8	10.9	11.0	10.4	11.0	9.7	14.3	-15.2
	TES	27.4 ± 0.8	18.6	18.4	19.0	27.6	23.9	24.7	25.0	26.2	25.5	23.1	27.9	-23.1
$BzCr(CO)_2L$	η^2-2,3-dihydrofuran	21.0 ± 1.0	18.0	20.1	22.8	24.3	19.8	20.1	20.3	19.0	17.9	17.3	21.7	-9.1
	η^2-3-hexyne	22.8 ± 0.4	19.0	21.3	26.2	24.1	20.2	20.5	20.6	19.3	18.9	18.5	24.2	-8.2
	η^2-benzene	11.5 ± 0.9	4.9	10.3	13.3	10.4	5.7	6.3	6.4	5.1	7.3	6.3	10.2	-9.8
	TES	24.3 ± 1.2	16.7	18.7	23.0	23.0	17.9	19.3	19.7	19.6	19.2	18.1	23.7	-12.0
	THF	21.4 ± 0.8	14.8	20.1	21.5	18.9	14.7	15.2	15.2	14.4	17.8	16.8	19.0	2.3
$Cr(CO)_5L$	η^2-benzene	11.4 ± 1.1	8.7	14.0	17.4	13.1	8.8	9.7	9.8	9.3	11.6	10.5	13.3	-4.8
	η^2-3-hexyne	18.3 ± 0.7	17.9	20.4	25.4	20.8	16.9	17.7	17.9	17.7	18.3	17.4	20.7	-7.4
$CpRe(CO)_2L$	heptane	13.7 ± 0.2	10.8	13.7	17.6	13.6	11.3	12.8	12.8	13.6	14.2	13.6	16.3	1.7
$(DMP)Mn(CO)_2L$	THF	22.1 ± 0.5	18.6	23.1	24.3	22.2	19.0	19.4	19.4	19.0	22.1	21.0	22.9	5.0
	η^2-benzene	14.9 ± 1.4	10.4	13.5	15.1	17.3	13.8	13.5	13.6	13.0	13.7	12.2	16.5	-13.7
	bromohexane	21.1 ± 0.4	13.9	15.7	16.8	19.8	17.7	17.5	17.6	16.7	16.7	16.1	17.9	-3.2
$TpRe(CO)_2L$	THF	23.9 ± 0.9	23.4	29.0	32.1	27.3	21.4	22.8	22.8	23.3	28.3	26.7	30.3	13.2
		MSE	-5.5	-3.1	-1.1	0.3	-3.3	-3.0	-2.8	-3.1	-2.6	-3.7	-0.2	-28.2
		MUE	5.5	4.1	4.4	1.8	3.4	3.0	2.9	3.2	3.1	3.9	2.0	28.2
		RMSD	6.2	5.4	5.5	2.0	3.9	3.6	3.5	3.8	3.8	4.6	2.5	30.4
		MAXD	10.8	11.1	10.7	3.4	6.9	7.3	7.1	7.0	8.0	9.7	6.4	50.5

Table S7: Approximate BDEs ($_{Frozen}BDE^{\omega B97XD}$) calculated on ωB97XD geometries using DFT functionals/methods listed in **Table S1** for subset of complexes

			LSDA	GGA					HGGA					MGGA				
Complex	Ligand L	Expt	SVWN	B97D	BLYP	MPW PW91	PBE PBE	PW91 PW91	APF	APFD	B3LYP	BH& HLYP	PBE1 PBE	BB95	M06-L	MPW B95	tHCTH	TPSS TPSS
$CpMn(CO)_2L$	η^2-2,3-dihydrofuran	28.4 ± 1.0	53.1	33.7	18.7	28.7	31.8	32.2	25.5	40.9	17.7	11.3	27.2	29.6	29.5	32.6	21.1	28.8
	chloropropane	16.0 ± 0.6	31.1	17.6	12.1	16.5	18.3	18.9	14.8	25.7	11.9	9.6	15.8	16.3	17.2	18.5	12.1	16.8
	η^2-cycloheptene	28.5 ± 0.8	50.1	31.9	14.7	24.9	28.1	28.6	22.0	40.4	14.0	7.9	23.8	26.3	26.9	29.4	16.9	25.5
	η^2-cyclooctene	34.9 ± 0.7	54.0	35.1	18.5	29.0	32.1	32.5	26.2	43.6	18.0	11.8	28.0	30.0	30.3	33.0	21.1	29.5
	η^2-furan	21.9 ± 1.0	40.0	24.4	11.8	19.9	22.4	22.9	17.4	32.5	11.2	6.7	18.8	20.3	20.4	22.8	13.5	20.4
	$S(n\text{-}Bu)_2$	36.0 ± 1.0	53.3	36.8	25.3	32.9	35.4	36.0	30.2	45.0	24.6	19.8	31.5	32.5	32.8	35.2	27.0	32.6
	tetrahydrothiophene	37.0	53.0	35.2	26.0	33.5	35.8	36.3	30.4	42.3	25.0	19.7	31.6	32.8	32.0	35.2	27.9	32.9
	THF	24.0 ± 3.0	33.5	23.0	14.6	17.4	19.5	20.3	17.4	31.1	15.8	15.7	18.6	17.4	22.1	19.9	13.2	18.6
	thiophene	19.5	38.4	23.0	15.7	21.9	23.9	24.4	19.7	30.0	15.2	11.5	20.8	21.1	20.4	23.3	17.1	21.9
	toluene	14.2 ± 0.8	29.8	19.5	4.9	11.4	13.9	14.6	9.6	28.7	4.9	2.5	11.1	12.2	15.5	15.0	5.7	11.9
	TES	27.4 ± 0.8	52.2	31.3	14.3	25.9	29.5	29.7	22.8	42.1	13.7	6.2	24.7	27.4	25.7	30.6	17.6	24.6
$BzCr(CO)_2L$	η^2-2,3-dihydrofuran	21.0 ± 1.0	42.9	26.4	11.5	20.2	23.2	23.8	18.5	34.3	11.6	8.9	20.3	21.7	23.0	24.7	12.7	20.8
	η^2-3-hexyne	22.8 ± 0.4	43.9	27.1	11.7	20.7	23.8	24.5	18.9	39.9	11.8	8.9	20.8	21.6	22.7	24.9	13.6	21.2
	η^2-benzene	11.5 ± 0.9	18.7	12.8	0.0	4.5	6.7	7.4	4.1	21.9	0.7	0.6	5.5	5.9	10.4	8.4	0.5	5.2
	TES	24.3 ± 1.2	43.2	24.9	8.1	18.6	22.1	22.5	17.4	38.0	8.9	6.0	19.5	20.6	20.7	23.8	10.1	18.1
	THF	21.4 ± 0.8	30.2	20.6	12.3	15.0	17.1	17.8	14.4	28.5	12.8	12.3	15.6	15.3	19.5	17.8	11.0	15.9
$Cr(CO)_5L$	η^2-benzene	11.4 ± 1.1	21.8	14.6	2.7	7.5	9.7	10.3	7.8	23.5	4.1	4.2	9.2	8.7	13.0	11.2	3.5	8.4
	η^2-3-hexyne	18.3 ± 0.7	38.1	20.6	7.4	16.0	19.1	19.8	16.0	31.5	9.0	7.9	18.0	17.3	19.5	20.6	9.0	17.2
$CpRe(CO)_2L$	heptane	13.7 ± 0.2	24.8	15.3	5.6	10.7	12.4	12.9	11.8	26.4	7.8	8.7	13.0	10.0	11.4	11.9	7.2	11.1
$(DMP)Mn(CO)_2L$	THF	22.1 ± 0.5	35.3	24.6	16.4	19.2	21.3	22.0	18.3	31.6	16.7	15.6	19.4	19.1	22.7	21.6	14.9	20.2
	η^2-benzene	14.9 ± 1.4	33.5	22.3	7.8	14.3	16.9	17.4	11.4	29.7	6.7	3.3	12.8	15.7	17.2	18.4	8.9	14.5
	bromohexane	21.1 ± 0.4	34.0	20.4	13.5	18.8	20.8	21.3	16.3	28.1	12.6	9.5	17.3	18.8	18.9	20.9	14.3	18.9
$TpRe(CO)_2L$	THF	23.9 ± 0.9	35.8	30.5	15.8	18.9	21.1	22.1	20.5	40.2	18.5	20.5	22.0	19.0	26.5	21.8	15.4	20.8
		MSE	16.4	2.5	-9.8	-2.9	-0.4	0.2	-4.5	11.4	-9.6	-12.4	-3.0	-2.4	-0.7	0.3	-8.7	-2.6
		MUE	16.4	2.9	9.8	3.2	2.0	1.9	4.5	11.4	9.6	12.4	3.1	2.8	2.0	2.1	8.7	2.9
		RMSD	17.1	3.5	10.3	3.8	2.5	2.4	5.0	11.8	10.2	13.5	3.7	3.4	2.3	2.5	9.1	3.4
		MAXD	24.8	7.4	16.4	7.0	4.8	4.9	8.7	17.1	16.9	23.1	6.9	6.6	5.0	4.2	14.2	6.3

Complex	Ligand L	Expt.	HMGGA					RS-HGGA						Ab Initio
			BMK	M06-2X	M06-HF	M06	TPSSh	HSE2PBE	HSHE1PBE	LC-ωPBE	ωB97	ωB97X	ωB97XD	HF
$CpMn(CO)_2L$	η^2-2,3-dihydrofuran	28.4 ± 1.0	22.7	22.3	22.0	30.8	27.1	26.7	26.9	27.2	25.6	24.0	27.9	-13.0
	chloropropane	16.0 ± 0.6	13.4	15.9	17.2	17.7	15.8	16.0	16.1	15.1	16.1	15.5	16.5	-1.3
	η^2-cycloheptene	28.5 ± 0.8	19.9	20.4	20.7	27.5	23.9	23.4	23.5	23.9	22.7	21.1	26.2	-16.5
	η^2-cyclooctene	34.9 ± 0.7	23.9	23.7	24.2	31.6	27.9	27.5	27.7	28.4	26.7	25.1	29.9	-12.9
	η^2-furan	21.9 ± 1.0	14.9	15.9	17.2	21.9	19.0	18.6	18.7	18.6	17.4	16.3	19.7	-11.6
	$S(n\text{-}Bu)_2$	36.0 ± 1.0	26.4	26.9	27.9	33.9	31.2	31.5	31.5	31.1	30.5	29.6	33.1	1.6
	tetrahydrothiophene	37.0	26.3	25.6	26.2	33.2	31.4	31.6	31.7	31.1	30.1	29.3	31.9	1.2
	THF	24.0 ± 3.0	18.8	23.6	25.5	22.3	18.3	19.2	19.1	18.9	22.0	21.0	23.0	6.7
	thiophene	19.5	16.7	16.2	17.6	21.7	20.7	20.8	20.9	20.5	19.9	19.2	21.0	-3.1
	toluene	14.2 ± 0.8	8.8	13.5	15.8	15.8	10.8	11.1	11.2	10.5	12.1	10.9	15.0	-10.2
	TES	27.4 ± 0.8	18.7	18.1	18.9	27.0	23.2	24.1	24.4	25.6	24.8	22.6	27.5	-21.4
$BzCr(CO)_2L$	η^2-2,3-dihydrofuran	21.0 ± 1.0	17.7	20.1	22.9	24.0	19.7	19.9	20.1	18.8	17.8	17.2	21.7	-8.1
	η^2-3-hexyne	22.8 ± 0.4	18.9	21.0	25.5	23.7	20.0	20.5	20.6	19.1	18.7	18.4	24.1	-8.6
	η^2-benzene	11.5 ± 0.9	4.6	10.4	12.7	9.8	4.8	5.7	5.7	4.8	7.9	6.8	10.3	-7.1
	TES	24.3 ± 1.2	16.2	18.2	22.4	22.2	17.3	18.9	19.2	19.2	18.7	17.7	23.3	-12.4
	THF	21.4 ± 0.8	15.5	20.1	21.0	19.3	15.3	16.1	16.0	15.2	18.3	17.5	19.6	3.6
$Cr(CO)_5L$	η^2-benzene	11.4 ± 1.1	8.5	13.9	16.7	12.7	8.3	9.3	9.4	8.9	11.8	10.6	13.3	-3.5
	η^2-3-hexyne	18.3 ± 0.7	17.6	20.0	24.9	20.5	16.8	17.6	17.8	17.5	18.0	17.2	20.5	-7.4
$CpRe(CO)_2L$	heptane	13.7 ± 0.2	10.7	13.5	17.7	13.4	11.5	13.0	13.0	13.8	14.2	13.6	16.4	1.3
$(DMP)Mn(CO)_2L$	THF	22.1 ± 0.5	19.1	23.5	24.7	22.7	19.4	19.9	19.9	19.5	22.5	21.5	23.3	5.8
	η^2-benzene	14.9 ± 1.4	10.3	14.1	16.0	16.8	13.0	12.9	13.0	12.3	13.9	12.4	16.4	-10.1
	bromohexane	21.1 ± 0.4	14.0	16.1	17.2	19.6	17.6	17.4	17.5	16.6	16.9	16.3	17.9	-2.1
$TpRe(CO)_2L$	THF	23.9 ± 0.9	23.2	28.9	31.9	27.0	21.1	22.6	22.6	23.2	28.1	26.5	30.1	13.2
		MSE	-5.5	-3.2	-1.2	0.0	-3.5	-3.0	-2.9	-3.2	-2.6	-3.6	-0.2	-27.4
		MUE	5.5	4.1	4.5	1.8	3.6	3.1	3.1	3.3	3.1	3.9	2.0	27.4
		RMSD	6.3	5.4	5.5	2.0	4.1	3.7	3.6	3.9	3.8	4.6	2.6	29.6
		MAXD	11.0	11.4	10.8	3.8	7.0	7.4	7.2	6.7	8.2	9.8	6.2	48.8

Table S8: BDEs calculated at M06 reference geometries for full database (**Table 1**) for all DFT functionals and methods (**Table 2**) used in the benchmark study.

			LSDA		GGA												
Complex	Ligand L	Expt.	SVWN	SVWN5	B97D	B97D3	BLYP	BLYP-GD2	BLYP-GD3	BLYP-GD3BJ	BP86	BP86-GD2	BP86-GD3	BP86-GD3BJ	BPBE	BPE-GD3	BPE-GD3BJ
$CpMn(CO)_2L$	η^2-2,3-dihydrofuran	28.4 ± 1.0	53.4	52.3	33.8	31.6	18.5	34.7	30.2	31.9	28.2	42.3	39.1	39.6	26.4	39.7	40.7
	chloropropane	16.0 ± 0.6	31.4	30.8	17.7	19.4	12.3	19.2	19.5	21.0	16.5	22.5	23.3	24.2	14.7	22.9	24.1
	η^2-cycloheptene	28.5 ± 0.8	50.3	49.1	32.0	29.2	14.8	33.2	28.3	29.8	24.5	40.6	37.2	37.6	22.6	37.9	38.8
	η^2-cyclooctene	34.9 ± 0.7	54.0	52.9	35.3	32.7	18.5	36.1	31.5	33.0	28.5	43.9	40.6	41.0	26.7	41.4	42.2
	η^2-furan	21.9 ± 1.0	41.0	40.0	24.6	23.3	11.6	25.6	21.7	23.9	19.7	31.9	29.2	30.3	18.0	29.6	31.3
	$S(n\text{-}Bu)_2$	36.0 ± 1.0	53.0	52.1	36.7	38.9	25.2	37.5	37.0	39.7	32.3	43.0	43.4	45.2	30.5	43.9	46.2
	tetrahydrothiophene	37.0	53.5	52.6	35.9	38.5	26.7	36.6	36.6	39.3	33.6	42.3	42.9	44.9	32.0	43.2	45.7
	THF	24.0 ± 3.0	33.5	32.9	23.0	25.4	14.7	28.7	27.7	27.6	17.6	30.5	30.2	29.6	14.9	29.5	29.0
	thiophene	19.5	37.7	36.9	22.9	25.9	14.9	23.8	23.8	27.1	20.6	28.5	29.1	31.7	19.0	29.2	32.4
	toluene	14.2 ± 0.8	32.0	31.1	19.5	17.8	4.0	20.6	16.9	18.8	11.1	25.6	23.2	24.3	9.0	23.7	25.2
	TES	27.4 ± 0.8	53.3	52.2	32.1	33.0	14.9	32.4	29.4	33.0	26.0	41.4	39.6	42.0	24.3	40.8	43.9
$BzCr(CO)_2L$	η^2-2,3-dihydrofuran	21.0 ± 1.0	43.7	42.7	26.6	24.9	11.3	28.0	22.8	25.6	19.9	34.5	30.6	32.1	17.9	31.0	33.2
	η^2-3-hexyne	22.8 ± 0.4	43.7	42.6	27.2	28.3	11.6	28.2	25.1	28.8	19.9	34.5	32.6	35.1	17.8	33.2	36.6
	η^2-benzene	11.5 ± 0.9	21.6	20.9	13.6	13.7	0.0	14.6	11.1	14.6	5.1	17.8	15.5	18.0	3.1	15.7	19.0
	TES	24.3 ± 1.2	43.6	42.6	25.5	27.3	8.8	26.4	23.6	27.9	18.4	33.8	32.2	35.4	16.6	33.3	37.3
	THF	21.4 ± 0.8	30.0	29.4	20.5	23.2	11.2	26.1	23.9	25.2	14.2	27.9	26.5	27.0	11.6	25.8	26.7
$Cr(CO)_5L$	η^2-benzene	11.4 ± 1.1	23.3	22.7	14.8	17.6	2.5	15.6	13.7	18.3	7.4	18.9	17.9	21.4	5.6	18.3	22.7
	η^2-3-hexyne	18.3 ± 0.7	38.5	37.5	20.8	20.5	7.3	22.2	18.8	21.4	15.4	28.4	26.1	27.8	13.2	26.2	28.7
$CpRe(CO)_2L$	heptane	13.7 ± 0.2	24.1	23.5	15.2	14.1	5.8	15.5	13.4	14.5	10.5	18.9	17.6	18.3	9.0	17.5	18.4
$(DMP)Mn(CO)_2L$	THF	22.1 ± 0.5	34.8	34.2	24.2	26.5	15.9	29.9	28.5	28.7	18.9	31.8	31.2	30.8	16.2	30.4	30.2
	η^2-benzene	14.9 ± 1.4	36.1	35.2	23.0	21.3	8.0	23.9	19.9	22.0	15.1	29.1	26.3	27.6	13.1	26.7	28.5
	bromohexane	21.1 ± 0.4	34.6	33.9	20.5	22.1	13.4	21.4	21.5	23.4	18.6	25.6	26.3	27.7	17.1	26.3	28.0
$TpRe(CO)_2L$	THF	23.9 ± 0.9	36.0	35.4	30.9	26.9	16.3	35.9	30.7	28.5	19.4	37.2	33.5	31.1	16.5	32.6	30.1
$CpRu(CO)(Cl)L$	η^2-cyclopentene	18.8 ± 1.1	36.1	35.0	22.2	19.8	4.6	22.5	16.9	20.0	13.5	29.2	25.1	26.8	11.8	26.0	28.3
	η^2-cyclohexene	17.2 ± 1.4	32.2	31.2	18.8	16.9	1.6	19.4	14.7	17.5	10.1	25.7	22.4	24.1	8.1	23.2	25.4
	η^2-cyclooctene	21.0 ± 0.6	35.7	34.6	22.2	20.4	4.6	22.4	17.7	20.5	13.4	29.0	25.8	27.4	11.6	26.6	28.9
	THF	13.7 ± 0.3	22.5	21.8	14.3	17.1	4.0	19.3	17.3	18.5	7.2	21.3	20.2	20.6	4.7	19.9	20.5
$(\mu\text{-}pdt)Fe_2(CO)_5L$	η^2-3-hexyne	20.9 ± 0.4	39.9	38.8	21.6	21.0	5.7	22.9	20.9	21.8	14.8	29.8	29.1	29.1	12.4	29.6	30.2
	η^2-cyclohexene	19.7 ± 0.6	37.3	36.2	21.3	17.3	3.7	22.8	18.8	18.3	12.7	29.5	27.0	25.7	10.5	27.7	26.7
	η^2-2,3-dihydrofuran	20.9 ± 1.6	39.2	38.1	21.9	19.0	7.1	23.2	20.0	19.8	15.8	29.9	28.0	27.0	13.7	28.5	27.7
		MUE	16.7	15.8	2.7	2.7	10.9	4.1	2.2	3.5	4.0	9.3	7.5	8.6	5.9	7.8	9.3
		MSE	16.7	15.8	2.4	2.2	-10.9	4.1	1.2	3.1	-3.9	9.3	7.5	8.6	-5.9	7.8	9.3
		RMSD	17.3	16.4	3.3	3.3	11.4	4.8	2.8	4.0	4.6	9.7	7.8	8.9	6.5	8.1	9.8
		MAXD	25.9	24.8	8.1	6.4	16.4	12.0	6.8	7.6	7.6	14.2	12.2	14.6	9.8	13.4	16.5

Complex	Ligand L	Expt.	GGA													
			BPW91	G96LYP	HCTH	MPW LYP	MPW PBE	MPW PW91	N12	OLYP	PBEPBE	PBEPBE-GD2	PBEPBE-GD3	PBEPBE-GD3BJ	PW91 PW91	SOGGA11
$CpMn(CO)_2L$	η^2-2,3-dihydrofuran	28.4 ± 1.0	25.7	15.8	18.5	21.4	29.3	28.7	28.1	15.6	31.8	41.9	37.4	38.4	32.2	36.1
	chloropropane	16.0 ± 0.6	14.5	9.5	10.2	14.4	16.9	16.7	15.3	7.3	18.5	22.8	22.2	22.8	19.1	18.2
	η^2-cycloheptene	28.5 ± 0.8	21.9	11.7	14.0	17.8	25.7	25.0	24.4	10.8	28.3	39.8	35.1	35.9	28.7	31.5
	η^2-cyclooctene	34.9 ± 0.7	26.0	15.7	18.4	21.5	29.7	29.0	28.4	15.4	32.2	43.2	38.7	39.5	32.6	36.3
	η^2-furan	21.9 ± 1.0	17.5	9.0	10.6	14.1	20.7	20.1	19.3	8.2	22.8	31.5	27.7	28.9	23.2	26.4
	$S(n\text{-}Bu)_2$	36.0 ± 1.0	30.1	22.2	24.7	27.9	33.2	32.8	31.3	21.1	35.3	43.0	41.5	42.6	35.9	37.6
	tetrahydrothiophene	37.0	31.6	24.1	26.3	29.1	34.5	34.1	32.7	23.1	36.4	42.6	41.5	42.6	36.9	37.7
	THF	24.0 ± 3.0	14.9	11.0	11.3	17.2	17.5	17.5	19.9	7.1	19.5	29.8	27.9	28.0	20.3	21.7
	thiophene	19.5	18.7	12.3	13.6	17.1	21.3	21.0	19.6	10.7	23.0	28.6	27.6	29.0	23.6	24.3
	toluene	14.2 ± 0.8	8.7	0.5	2.6	6.8	11.9	11.6	10.1	-1.2	14.4	24.7	20.9	21.8	14.9	18.6
	TES	27.4 ± 0.8	23.6	11.6	16.8	18.0	27.5	26.8	26.0	12.4	30.5	41.5	37.9	39.6	30.7	30.8
$BzCr(CO)_2L$	η^2-2,3-dihydrofuran	21.0 ± 1.0	17.4	8.1	9.8	14.3	20.9	20.4	19.7	6.8	23.5	33.9	29.0	30.6	24.0	28.7
	η^2-3-hexyne	22.8 ± 0.4	17.3	7.8	10.8	14.8	21.1	20.6	19.5	7.1	23.8	34.2	30.7	32.6	24.4	30.9
	η^2-benzene	11.5 ± 0.9	2.9	-3.6	-1.8	2.6	5.7	5.5	4.1	-5.8	7.9	17.0	13.6	15.3	8.5	11.0
	TES	24.3 ± 1.2	16.0	5.1	9.1	12.0	19.9	19.3	18.5	4.9	22.8	33.8	30.2	32.4	23.2	25.7
	THF	21.4 ± 0.8	11.6	7.3	7.9	13.8	14.2	14.2	16.3	3.6	16.3	27.2	24.6	25.3	17.1	19.4
$Cr(CO)_5L$	η^2-benzene	11.4 ± 1.1	5.4	-1.1	1.3	5.0	8.1	8.0	7.0	-2.6	10.3	18.4	15.9	18.0	10.9	11.7
	η^2-3-hexyne	18.3 ± 0.7	12.7	3.3	6.1	10.5	16.5	16.0	15.7	2.4	19.2	28.5	25.1	26.4	19.8	22.6
$CpRe(CO)_2L$	heptane	13.7 ± 0.2	8.7	3.6	4.5	7.7	10.9	10.6	9.4	1.7	12.2	18.3	16.3	16.7	12.8	10.7
$(DMP)Mn(CO)_2L$	THF	22.1 ± 0.5	16.2	12.2	12.3	18.4	18.8	18.7	20.7	8.3	20.8	31.1	29.2	29.3	21.6	22.7
	η^2-benzene	14.9 ± 1.4	12.7	4.8	6.7	10.7	15.9	15.5	14.2	2.9	18.2	28.1	24.3	25.3	18.7	20.0
	bromohexane	21.1 ± 0.4	16.8	10.9	12.3	15.6	19.3	19.0	17.4	9.3	21.0	25.9	25.1	25.8	21.5	23.4
$TpRe(CO)_2L$	THF	23.9 ± 0.9	16.5	12.0	13.6	19.1	19.3	19.3	22.2	8.2	21.5	35.3	31.1	30.2	22.5	21.9
$CpRu(CO)(Cl)L$	η^2-cyclopentene	18.8 ± 1.1	11.2	1.6	3.8	7.4	14.7	14.2	13.9	0.9	17.0	28.2	23.0	24.6	17.6	20.5
	η^2-cyclohexene	17.2 ± 1.4	7.6	-1.6	-0.2	4.5	11.1	10.6	10.0	-3.3	13.4	24.6	19.8	21.3	14.1	14.5
	η^2-cyclooctene	21.0 ± 0.6	11.1	1.5	3.5	7.4	14.5	14.0	13.6	0.4	16.8	28.0	23.4	24.7	17.4	18.3
	THF	13.7 ± 0.3	4.7	0.2	0.9	6.5	7.3	7.3	9.6	-3.3	9.3	20.5	17.7	18.4	10.2	9.4
$(\mu\text{-}pdt)Fe_2(CO)_5L$	η^2-3-hexyne	20.9 ± 0.4	11.9	1.6	4.6	9.1	15.9	15.4	14.7	0.6	18.9	29.6	26.9	27.3	19.5	23.2
	η^2-cyclohexene	19.7 ± 0.6	10.0	-0.1	1.9	6.9	13.8	13.3	12.9	-1.7	16.7	28.6	24.5	24.4	17.2	19.6
	η^2-2,3-dihydrofuran	20.9 ± 1.6	13.2	3.8	5.3	10.1	16.8	16.3	15.6	2.0	19.4	29.5	26.0	26.0	19.9	21.5
		MUE	6.3	14.2	12.2	8.2	3.4	3.7	3.9	15.8	2.2	8.8	5.6	6.6	2.0	2.9
		MSE	-6.3	-14.2	-12.2	-8.2	-3.1	-3.5	-3.9	-15.8	-0.8	8.8	5.6	6.6	-0.2	1.6
		RMSD	6.8	14.6	12.6	8.8	4.0	4.3	4.4	16.1	2.6	9.2	6.0	7.0	2.4	3.6
		MAXD	9.9	19.8	17.8	13.6	7.2	7.2	7.4	21.4	5.1	14.1	10.5	12.2	4.3	8.1

Complex	Ligand L	Expt.	HGGA														
			APF	APFD	B1LYP	B3LYP	B3LYP-GD2	B3LYP-GD3	B3LYP-GD3BJ	B3P86	B3PW91	B3PW91-GD3	B3PW91-GD3BJ	B97-1	B97-2	B98	BH&H
$CpMn(CO)_2L$	η^2-2,3-dihydrofuran	28.4 ± 1.0	25.6	40.9	15.2	17.6	31.7	27.1	28.7	26.2	23.1	33.9	34.9	23.0	19.8	21.4	34.3
	chloropropane	16.0 ± 0.6	14.9	25.9	10.9	12.0	18.0	18.0	19.3	15.7	13.5	20.2	21.3	14.2	11.6	13.4	22.1
	η^2-cycloheptene	28.5 ± 0.8	22.1	40.5	11.7	14.1	30.2	25.2	26.6	22.9	19.6	32.1	33.0	19.8	16.2	18.2	31.4
	η^2-cyclooctene	34.9 ± 0.7	26.3	43.7	15.6	18.0	33.4	28.7	30.0	26.9	23.8	35.8	36.6	23.7	20.4	22.1	35.3
	η^2-furan	21.9 ± 1.0	17.6	32.4	9.0	10.9	23.2	19.3	21.2	18.2	15.5	24.9	26.4	15.6	12.6	14.3	25.5
	$S(n\text{-}Bu)_2$	36.0 ± 1.0	30.0	44.9	22.6	24.5	35.3	34.3	36.6	30.9	28.1	39.1	41.1	28.4	25.6	27.2	37.8
	tetrahydrothiophene	37.0	31.0	43.0	23.7	25.6	34.3	33.8	36.2	31.9	29.3	38.5	40.6	29.3	26.8	28.2	37.8
	THF	24.0 ± 3.0	17.5	31.2	15.4	15.9	28.7	27.2	27.4	18.5	15.7	28.2	28.0	17.3	14.0	16.6	28.3
	thiophene	19.5	18.9	30.3	13.1	14.5	22.3	21.9	24.8	19.7	17.3	25.7	28.3	17.8	15.2	16.9	26.0
	toluene	14.2 ± 0.8	9.4	29.0	2.0	3.7	18.1	14.2	16.0	10.0	7.1	19.1	20.4	8.2	4.6	6.9	18.6
	TES	27.4 ± 0.8	23.5	42.9	11.2	13.9	29.3	25.9	29.0	23.8	20.7	34.2	36.8	20.2	17.4	18.0	31.3
$BzCr(CO)_2L$	η^2-2,3-dihydrofuran	21.0 ± 1.0	18.7	34.5	9.6	11.4	26.0	20.8	23.3	19.1	16.1	26.6	28.7	16.7	12.9	15.3	29.8
	η^2-3-hexyne	22.8 ± 0.4	18.9	40.1	10.0	11.7	26.3	22.6	26.2	19.3	16.2	28.6	31.7	17.7	13.5	16.2	30.1
	η^2-benzene	11.5 ± 0.9	4.8	22.5	-0.4	0.6	13.3	9.6	12.7	5.1	2.7	12.9	15.8	4.4	1.0	3.3	14.0
	TES	24.3 ± 1.2	17.9	38.7	7.5	9.4	24.7	21.4	25.3	17.9	14.9	28.5	32.0	15.7	12.0	13.9	28.9
	THF	21.4 ± 0.8	13.5	28.1	11.1	11.8	25.3	22.8	24.0	14.4	11.7	24.0	24.8	13.6	10.1	12.7	23.7
$Cr(CO)_5L$	η^2-benzene	11.4 ± 1.1	8.1	23.6	3.1	3.9	15.3	13.1	17.0	8.3	6.0	16.3	20.1	7.8	4.6	6.7	17.6
	η^2-3-hexyne	18.3 ± 0.7	16.0	31.6	7.6	8.9	22.0	18.2	20.6	16.2	13.1	23.7	25.8	14.9	10.5	13.4	28.6
$CpRe(CO)_2L$	heptane	13.7 ± 0.2	11.6	25.9	7.4	7.9	16.3	14.2	15.2	11.9	10.0	17.1	17.8	10.6	8.4	10.1	20.6
$(DMP)Mn(CO)_2L$	THF	22.1 ± 0.5	17.7	31.3	15.4	16.2	29.0	27.3	27.6	18.8	16.1	28.4	28.3	17.7	14.3	16.9	27.5
	η^2-benzene	14.9 ± 1.4	12.1	30.9	4.7	6.6	20.6	16.5	18.4	13.0	10.1	21.2	22.8	10.8	7.6	9.5	20.4
	bromohexane	21.1 ± 0.4	16.4	28.5	11.0	12.5	19.4	19.3	20.9	17.1	14.9	22.5	23.9	15.3	12.9	14.4	22.7
$TpRe(CO)_2L$	THF	23.9 ± 0.9	20.7	40.6	18.5	18.8	36.5	31.4	29.7	21.6	18.6	32.6	30.5	20.8	17.3	20.0	33.8
$CpRu(CO)(Cl)L$	η^2-cyclopentene	18.8 ± 1.1	16.5	44.3	7.4	8.3	24.0	18.6	21.1	16.3	13.5	24.9	27.1	14.5	10.8	13.3	30.6
	η^2-cyclohexene	17.2 ± 1.4	12.3	41.1	3.8	4.8	20.4	15.6	18.1	12.4	9.4	21.6	23.7	10.8	6.8	9.6	26.1
	η^2-cyclooctene	21.0 ± 0.6	16.3	39.4	7.5	8.4	24.0	19.4	21.7	16.3	13.4	25.6	27.6	14.5	10.8	13.4	30.6
	THF	13.7 ± 0.3	9.5	32.0	7.1	7.1	21.1	18.9	19.9	10.1	7.4	20.3	21.0	9.7	6.1	9.0	22.4
$(\mu\text{-}pdt)Fe_2(CO)_5L$	η^2-3-hexyne	20.9 ± 0.4	15.2	35.1	5.8	7.5	22.5	20.1	20.8	15.6	12.1	26.3	26.7	14.1	9.2	12.4	27.3
	η^2-cyclohexene	19.7 ± 0.6	13.4	38.0	4.1	5.6	22.4	18.4	17.8	13.7	10.4	24.6	23.7	11.9	7.3	10.2	25.8
	η^2-2,3-dihydrofuran	20.9 ± 1.6	15.5	38.0	6.7	8.3	22.4	19.2	18.8	16.0	12.9	25.0	24.3	14.0	9.8	12.5	26.9
		MUE	4.5	13.4	11.6	10.2	3.4	2.2	2.5	4.0	6.8	4.5	5.9	5.8	9.2	7.0	5.7
		MSE	-4.5	13.4	-11.6	-10.2	3.0	-0.1	1.6	-4.0	-6.8	4.5	5.9	-5.8	-9.2	-7.0	5.7
		RMSD	4.9	14.2	12.2	10.7	4.2	2.8	3.0	4.4	7.1	4.9	6.2	6.2	9.5	7.4	6.4
		MAXD	8.6	25.5	19.3	16.9	12.6	7.5	6.2	8.0	11.1	8.7	9.4	11.2	14.5	12.8	11.8

Complex	Ligand L	Expt.	HGGA											
			BH&HLYP	MPW1LYP	MPW1PBE	MPW1PW91	MPW3PBE	O3LYP	PBE1PBE	PBE1PBE-GD3	PBE1PBE-GD3BJ	PBEH1PBE	SOGGA11X	X3LYP
$CpMn(CO)_2L$	η^2-2,3-dihydrofuran	28.4 ± 1.0	11.1	17.4	25.3	24.6	25.8	15.8	27.2	33.2	33.5	27.0	18.9	18.7
	chloropropane	16.0 ± 0.6	9.6	12.5	14.7	14.5	15.2	8.0	16.0	19.8	20.2	16.2	11.8	12.9
	η^2-cycloheptene	28.5 ± 0.8	7.9	14.0	21.8	21.2	22.4	11.3	23.9	30.9	31.3	23.7	15.8	15.3
	η^2-cyclooctene	34.9 ± 0.7	11.8	17.8	26.0	25.4	26.5	15.9	28.0	34.9	35.1	27.8	19.7	19.1
	η^2-furan	21.9 ± 1.0	6.0	10.9	17.4	16.8	17.8	8.5	19.0	24.2	24.9	18.9	12.1	11.9
	$S(n\text{-}Bu)_2$	36.0 ± 1.0	19.8	24.7	29.7	29.3	30.4	21.5	31.4	37.8	38.5	31.4	24.6	25.5
	tetrahydrothiophene	37.0	20.4	25.6	30.7	30.3	31.4	23.2	32.2	37.4	38.3	32.2	25.3	26.5
	THF	24.0 ± 3.0	15.8	17.2	17.1	17.1	17.6	9.1	18.7	27.3	27.1	19.1	19.6	17.1
	thiophene	19.5	11.1	14.8	18.7	18.4	19.2	11.3	20.1	24.8	26.0	20.2	14.7	15.4
	toluene	14.2 ± 0.8	0.3	4.1	9.1	8.7	9.5	-0.4	10.9	17.7	18.3	11.0	4.8	4.8
	TES	27.4 ± 0.8	5.8	13.6	23.0	22.3	23.6	12.6	25.4	33.1	34.2	25.2	15.9	15.1
$BzCr(CO)_2L$	η^2-2,3-dihydrofuran	21.0 ± 1.0	8.5	11.9	18.5	18.0	18.7	7.8	20.5	26.3	27.3	20.3	14.1	12.7
	η^2-3-hexyne	22.8 ± 0.4	9.0	12.4	18.8	18.3	19.0	8.1	20.9	27.8	29.4	20.7	14.3	13.1
	η^2-benzene	11.5 ± 0.9	-0.1	1.6	4.6	4.4	4.7	-4.5	6.2	12.0	13.4	6.4	2.3	1.7
	TES	24.3 ± 1.2	6.3	9.9	17.7	17.1	17.8	6.0	20.0	27.7	29.3	19.8	13.1	10.8
	THF	21.4 ± 0.8	11.2	13.0	13.1	13.1	13.6	5.2	14.8	23.4	23.7	15.2	15.5	12.9
$Cr(CO)_5L$	η^2-benzene	11.4 ± 1.1	3.9	5.0	8.0	7.8	8.0	-0.9	9.6	15.5	17.2	9.8	6.4	5.0
	η^2-3-hexyne	18.3 ± 0.7	7.8	10.1	16.0	15.5	15.9	4.4	18.1	24.1	25.1	18.0	13.0	10.4
$CpRe(CO)_2L$	heptane	13.7 ± 0.2	8.7	8.8	11.7	11.5	11.5	3.6	12.8	17.0	17.2	12.9	10.1	8.8
$(DMP)Mn(CO)_2L$	THF	22.1 ± 0.5	15.0	17.3	17.3	17.3	17.9	9.8	18.9	27.5	27.3	19.3	19.3	17.3
	η^2-benzene	14.9 ± 1.4	2.3	6.7	11.7	11.4	12.4	3.0	13.5	19.9	20.5	13.6	7.2	7.6
	bromohexane	21.1 ± 0.4	9.1	12.7	16.1	15.8	16.7	9.5	17.4	21.7	22.3	17.5	12.1	13.3
$TpRe(CO)_2L$	THF	23.9 ± 0.9	20.6	20.6	20.5	20.5	20.6	11.0	22.2	32.0	30.9	22.8	24.4	20.2
$CpRu(CO)(Cl)L$	η^2-cyclopentene	18.8 ± 1.1	10.0	9.6	16.8	16.3	16.0	3.8	18.6	24.9	25.8	18.2	13.7	9.8
	η^2-cyclohexene	17.2 ± 1.4	6.1	6.0	12.6	12.1	12.0	-0.5	14.4	21.1	22.0	14.1	9.8	6.3
	η^2-cyclooctene	21.0 ± 0.6	10.3	9.7	16.7	16.2	15.9	3.4	18.4	25.4	26.2	18.2	14.1	9.9
	THF	13.7 ± 0.3	10.4	9.0	9.5	9.5	9.3	-0.3	11.0	19.8	20.0	11.4	13.5	8.5
$(\mu\text{-}pdt)Fe_2(CO)_5L$	η^2-3-hexyne	20.9 ± 0.4	4.5	8.4	15.0	14.5	15.1	2.5	17.3	25.5	25.6	17.2	11.1	9.0
	η^2-cyclohexene	19.7 ± 0.6	3.5	6.6	13.3	12.8	13.2	0.4	15.5	23.7	23.0	15.4	9.8	7.1
	η^2-2,3-dihydrofuran	20.9 ± 1.6	5.8	9.0	15.4	14.9	15.5	3.6	17.4	24.3	23.8	17.4	11.8	9.7
		MUE	12.5	9.5	4.7	5.0	4.4	14.5	2.9	3.8	4.4	2.9	7.6	9.0
		MSE	-12.5	-9.5	-4.7	-5.0	-4.4	-14.5	-2.9	3.8	4.4	-2.8	-7.6	-9.0
		RMSD	13.5	10.1	5.1	5.4	4.8	14.7	3.5	4.2	4.8	3.4	8.4	9.5
		MAXD	23.1	17.1	8.9	9.5	8.4	19.3	6.9	8.1	7.0	7.1	15.2	15.8

Complex	Ligand L	Expt	MGGA													
			BB95	M06-L	M11-L	MN12-L	MPW B95	MPW KCIS	PBE KCIS	tHCTH	TPSS KCIS	TPSS TPSS	TPSSTPSS-GD2	TPSSTPSS-GD3	TPSSTPSS-GD3BJ	VSXC
$CpMn(CO)_2L$	η^2-2,3-dihydrofuran	28.4 ± 1.0	29.7	29.6	20.2	29.1	32.7	25.7	28.2	20.9	26.3	28.9	42.3	36.8	37.5	48.8
	chloropropane	16.0 ± 0.6	16.5	17.2	13.1	16.8	18.7	15.0	16.6	12.2	15.8	17.0	22.8	22.1	22.7	29.3
	η^2-cycloheptene	28.5 ± 0.8	26.5	26.9	17.6	26.8	29.6	21.9	24.5	16.9	23.0	25.6	41.0	35.0	35.6	49.0
	η^2-cyclooctene	34.9 ± 0.7	30.1	30.4	21.5	30.4	33.0	25.9	28.4	21.0	26.8	29.5	44.2	38.5	39.1	50.1
	η^2-furan	21.9 ± 1.0	20.6	20.5	12.8	20.3	23.2	17.4	19.5	13.4	18.3	20.6	32.3	27.5	28.7	34.9
	$S(n\text{-}Bu)_2$	36.0 ± 1.0	32.5	32.8	25.1	32.4	35.2	30.6	32.7	26.6	30.8	32.5	42.7	40.8	42.1	50.6
	tetrahydrothiophene	37.0	33.4	32.7	25.0	31.8	35.9	32.0	33.9	28.3	31.9	33.5	41.7	40.4	41.8	46.1
	THF	24.0 ± 3.0	17.4	22.1	22.9	25.6	19.9	15.8	17.7	13.1	17.5	18.7	31.2	28.9	28.7	41.0
	thiophene	19.5	20.2	20.2	13.5	19.7	22.5	18.9	20.6	15.9	19.5	21.0	28.4	27.3	29.0	30.8
	toluene	14.2 ± 0.8	12.6	14.8	8.4	14.5	15.5	9.1	11.5	5.0	10.1	12.1	25.9	21.1	22.0	36.4
	TES	27.4 ± 0.8	28.5	26.4	12.6	27.9	31.7	25.2	28.2	18.1	23.7	25.4	40.0	35.6	37.4	54.5
$BzCr(CO)_2L$	η^2-2,3-dihydrofuran	21.0 ± 1.0	22.0	23.1	15.5	21.8	25.1	17.5	20.0	12.5	18.6	21.0	34.9	28.8	30.3	45.4
	η^2-3-hexyne	22.8 ± 0.4	21.7	23.0	16.3	21.3	25.0	17.7	20.4	13.4	18.9	21.3	35.1	30.7	32.8	48.2
	η^2-benzene	11.5 ± 0.9	6.9	10.6	6.4	10.7	9.5	3.6	5.7	0.4	4.9	6.4	18.5	14.2	16.1	32.3
	TES	24.3 ± 1.2	21.3	21.5	10.6	22.5	24.6	17.5	20.4	10.6	17.0	18.8	33.4	29.0	31.4	53.7
	THF	21.4 ± 0.8	14.8	19.4	19.1	22.0	17.5	12.6	14.7	9.6	14.2	15.3	28.6	25.3	26.0	41.0
$Cr(CO)_5L$	η^2-benzene	11.4 ± 1.1	9.3	13.3	9.5	13.9	11.9	6.0	8.1	3.3	7.6	9.1	20.0	16.8	19.4	33.7
	η^2-3-hexyne	18.3 ± 0.7	17.5	19.8	13.3	19.0	20.8	13.2	15.9	8.7	15.1	17.4	29.8	25.4	26.9	42.8
$CpRe(CO)_2L$	heptane	13.7 ± 0.2	10.0	11.7	9.3	13.0	11.9	9.0	10.4	7.2	9.8	11.1	19.1	16.5	16.9	21.7
$(DMP)Mn(CO)_2L$	THF	22.1 ± 0.5	18.6	22.2	22.7	25.1	21.2	17.0	19.0	14.2	18.6	19.7	32.3	29.9	29.7	40.7
	η^2-benzene	14.9 ± 1.4	16.8	17.4	9.8	16.3	19.5	13.1	15.4	9.4	13.7	15.6	28.9	23.9	25.0	38.3
	bromohexane	21.1 ± 0.4	18.9	18.8	12.1	17.6	21.1	17.2	18.9	14.3	17.8	19.1	25.7	24.8	25.6	31.2
$TpRe(CO)_2L$	THF	23.9 ± 0.9	19.5	26.8	27.9	30.9	22.3	17.5	19.7	15.6	20.0	21.2	38.4	32.8	31.3	50.2
$CpRu(CO)(Cl)L$	η^2-cyclopentene	18.8 ± 1.1	14.8	17.9	17.4	24.7	17.7	10.8	13.0	7.8	13.1	16.0	31.0	24.4	26.0	39.2
	η^2-cyclohexene	17.2 ± 1.4	10.9	14.2	13.0	20.4	13.9	7.3	9.6	4.4	9.6	12.3	27.2	21.3	22.8	35.0
	η^2-cyclooctene	21.0 ± 0.6	14.1	18.0	16.9	24.2	17.1	10.6	12.8	7.9	13.1	15.9	30.8	25.0	26.4	37.8
	THF	13.7 ± 0.3	7.6	14.4	18.8	23.6	10.2	5.2	7.1	3.8	8.4	9.9	23.6	20.3	20.8	35.7
$(\mu\text{-}pdt)Fe_2(CO)_5L$	η^2-3-hexyne	20.9 ± 0.4	16.5	20.5	13.9	22.9	20.0	12.1	15.0	7.4	14.3	16.9	31.3	27.7	28.0	47.1
	η^2-cyclohexene	19.7 ± 0.6	15.1	20.3	12.2	22.4	18.4	10.0	12.7	5.0	12.5	15.3	31.3	26.0	25.4	47.4
	η^2-2,3-dihydrofuran	20.9 ± 1.6	17.8	21.9	13.7	23.7	20.9	13.1	15.6	8.5	15.3	17.9	31.4	27.0	26.6	44.2
		MUE	3.3	1.7	6.5	2.5	2.1	5.9	3.9	9.7	4.7	3.0	9.9	5.9	6.9	19.7
		MSE	-2.8	-0.6	-5.8	0.8	0.0	-5.9	-3.7	-9.7	-4.7	-2.7	9.9	5.9	6.9	19.7
		RMSD	3.8	2.1	7.5	3.3	2.6	6.5	4.5	10.1	5.1	3.4	10.3	6.2	7.1	20.5
		MAXD	6.9	4.5	14.8	9.9	4.6	10.4	8.2	14.7	8.1	6.1	14.5	9.0	10.1	29.4

Complex	Ligand L	Expt	HMGGA									
			B1B95	BMK	BMK-GD3	BMK-GD3BJ	M05	M05-2X	MO6	M06-2X	M06-HF	TPSSh
$CpMn(CO)_2L$	η^2-2,3-dihydrofuran	28.4 ± 1.0	26.0	22.9	32.8	32.0	24.0	26.1	30.9	22.3	22.0	27.2
	chloropropane	16.0 ± 0.6	14.8	13.5	19.3	20.0	12.4	17.4	17.8	15.8	17.2	16.1
	η^2-cycloheptene	28.5 ± 0.8	23.1	20.2	31.2	30.6	20.2	23.9	27.7	20.4	20.9	24.0
	η^2-cyclooctene	34.9 ± 0.7	26.9	24.1	34.6	34.1	24.5	27.6	31.8	23.8	24.2	28.0
	η^2-furan	21.9 ± 1.0	17.7	14.9	23.4	23.5	15.2	18.8	22.1	15.4	16.5	19.2
	$S(n\text{-}Bu)_2$	36.0 ± 1.0	29.4	26.6	36.1	37.4	26.6	30.8	34.1	27.1	28.3	31.1
	tetrahydrothiophene	37.0	29.9	27.1	35.1	36.7	27.6	30.3	33.9	26.5	27.2	32.0
	THF	24.0 ± 3.0	17.8	18.9	30.3	29.4	15.7	24.1	22.5	23.7	25.8	18.3
	thiophene	19.5	18.1	16.5	23.8	26.0	15.4	19.4	22.1	16.5	18.4	19.9
	toluene	14.2 ± 0.8	10.3	8.1	18.4	18.8	7.2	13.8	15.8	12.0	14.3	10.8
	TES	27.4 ± 0.8	24.3	18.6	30.4	32.0	21.1	23.2	27.6	18.4	19.0	23.9
$BzCr(CO)_2L$	η^2-2,3-dihydrofuran	21.0 ± 1.0	20.2	18.0	27.5	27.7	15.8	22.6	24.3	20.1	22.8	19.8
	η^2-3-hexyne	22.8 ± 0.4	20.1	19.0	29.4	31.1	15.8	24.3	24.1	21.3	26.2	20.2
	η^2-benzene	11.5 ± 0.9	6.4	4.9	13.6	15.4	3.0	10.9	10.4	10.3	13.3	5.7
	TES	24.3 ± 1.2	19.8	16.7	28.5	30.8	13.9	21.8	23.0	18.7	23.0	17.9
	THF	21.4 ± 0.8	14.4	14.8	26.0	25.9	12.2	20.1	18.9	20.1	21.5	14.7
$Cr(CO)_5L$	η^2-benzene	11.4 ± 1.1	9.9	8.7	17.7	20.1	7.3	14.6	13.1	14.0	17.4	8.8
	η^2-3-hexyne	18.3 ± 0.7	17.9	17.9	26.7	27.4	14.1	22.6	20.8	20.4	25.4	16.9
$CpRe(CO)_2L$	heptane	13.7 ± 0.2	11.6	10.8	16.7	17.4	7.6	15.4	13.6	13.7	17.6	11.3
$(DMP)Mn(CO)_2L$	THF	22.1 ± 0.5	17.8	18.6	29.8	29.1	16.0	23.4	22.2	23.1	24.3	19.0
	η^2-benzene	14.9 ± 1.4	13.1	10.4	20.0	20.5	10.3	15.1	17.3	13.5	15.1	13.8
	bromohexane	21.1 ± 0.4	16.1	13.9	20.7	22.1	14.0	17.5	19.8	15.7	16.8	17.7
$TpRe(CO)_2L$	THF	23.9 ± 0.9	21.7	23.4	35.6	33.1	20.2	29.5	27.3	29.0	32.1	21.4
$CpRu(CO)(Cl)L$	η^2-cyclopentene	18.8 ± 1.1	18.0	15.4	26.0	26.5	11.1	23.0	19.9	19.2	28.5	16.6
	η^2-cyclohexene	17.2 ± 1.4	13.4	11.9	23.1	23.5	6.9	18.8	15.9	15.0	24.1	12.7
	η^2-cyclooctene	21.0 ± 0.6	17.4	15.8	26.8	27.3	11.1	23.0	20.2	19.3	28.9	16.5
	THF	13.7 ± 0.3	10.8	13.8	26.2	25.5	7.0	19.1	13.5	17.8	24.4	10.5
$(\mu\text{-}pdt)Fe_2(CO)_5L$	η^2-3-hexyne	20.9 ± 0.4	16.6	16.2	28.1	27.0	12.0	20.4	21.5	17.7	18.3	16.4
	η^2-cyclohexene	19.7 ± 0.6	15.5	14.4	26.8	24.1	10.8	18.6	21.2	16.8	17.9	14.9
	η^2-2,3-dihydrofuran	20.9 ± 1.6	17.3	15.8	26.6	24.0	12.7	19.5	22.3	17.8	18.7	17.2
		MUE	3.7	5.2	5.0	5.2	7.2	2.6	1.6	3.7	4.7	3.5
		MSE	-3.7	-5.1	4.8	5.1	-7.2	-0.4	0.3	-2.7	0.1	-3.5
		RMSD	4.2	5.8	5.8	5.9	7.5	3.3	1.9	4.9	5.8	3.9
		MAXD	8.0	10.8	12.5	11.8	10.4	7.3	3.4	11.1	10.7	6.9

Complex	Ligand L	Expt	RS-HGGA														
			CAM-B3LYP	CAM-B3LYP-GD3	CAM-B3LYP-GD3BJ	HISSbPBE	HSE2PBE	HSEH1PBE	LC-ωPBE	LC-ωPBE-GD3	LC-ωPBE-GD3BJ	M11	MN12SX	N12SX	ωB97	ωB97X	ωB97XD
$CpMn(CO)_2L$	η^2-2,3-dihydrofuran	28.4 ± 1.0	20.7	27.4	27.0	24.6	26.8	27.0	27.4	34.4	34.5	25.8	23.3	26.7	25.7	24.1	28.0
	chloropropane	16.0 ± 0.6	14.0	18.1	18.4	14.9	16.2	16.2	15.1	19.5	20.0	15.4	13.9	15.1	16.0	15.5	16.6
	η^2-cycloheptene	28.5 ± 0.8	17.4	25.1	24.8	21.3	23.5	23.7	24.1	32.3	32.4	23.9	20.8	23.6	22.9	21.3	26.4
	η^2-cyclooctene	34.9 ± 0.7	21.3	28.8	28.5	25.6	27.6	27.8	28.5	36.4	36.4	27.1	24.6	27.6	26.9	25.2	30.1
	η^2-furan	21.9 ± 1.0	13.5	19.3	19.4	17.0	18.7	18.9	18.9	25.0	25.5	17.0	15.5	18.6	17.4	16.3	19.7
	$S(n\text{-}Bu)_2$	36.0 ± 1.0	26.9	33.9	34.4	29.5	31.4	31.5	30.9	38.3	39.1	29.3	27.7	30.6	30.4	29.5	33.0
	tetrahydrothiophene	37.0	27.8	33.4	34.1	30.2	32.2	32.3	31.6	37.6	38.6	28.5	27.4	31.5	30.8	30.0	32.6
	THF	24.0 ± 3.0	19.3	28.3	27.7	22.6	19.2	19.2	19.0	28.5	28.1	26.3	23.4	21.8	22.1	21.1	23.1
	thiophene	19.5	16.8	21.9	23.1	18.8	20.1	20.2	20.0	25.4	26.9	17.0	16.2	19.3	19.7	19.0	20.9
	toluene	14.2 ± 0.8	6.3	13.7	13.8	9.7	10.9	11.0	10.4	18.3	18.8	12.1	10.1	10.2	11.0	9.7	14.3
	TES	27.4 ± 0.8	17.4	25.8	26.5	21.4	24.7	25.0	26.2	35.2	36.3	26.1	20.1	25.0	25.5	23.1	27.9
$BzCr(CO)_2L$	η^2-2,3-dihydrofuran	21.0 ± 1.0	14.3	20.9	21.1	18.7	20.1	20.3	19.0	26.0	26.7	20.5	17.7	20.1	17.9	17.3	21.7
	η^2-3-hexyne	22.8 ± 0.4	14.8	22.3	23.4	18.7	20.5	20.6	19.3	27.3	29.0	21.9	18.3	20.4	18.9	18.5	24.2
	η^2-benzene	11.5 ± 0.9	2.7	9.0	10.2	6.1	6.3	6.4	5.1	11.8	13.3	9.7	7.6	5.5	7.3	6.3	10.2
	TES	24.3 ± 1.2	12.9	21.4	22.7	17.5	19.3	19.7	19.6	28.5	30.3	22.4	16.5	19.7	19.2	18.1	23.7
	THF	21.4 ± 0.8	14.6	23.6	23.5	18.3	15.2	15.2	14.4	23.9	24.1	22.8	19.9	17.7	17.8	16.8	19.0
$Cr(CO)_5L$	η^2-benzene	11.4 ± 1.1	6.5	12.9	14.4	9.7	9.7	9.8	9.3	16.1	18.0	14.1	11.2	9.0	11.6	10.5	13.3
	η^2-3-hexyne	18.3 ± 0.7	12.9	19.3	20.0	16.9	17.7	17.9	17.7	24.5	25.6	20.8	16.3	17.9	18.3	17.4	20.7
$CpRe(CO)_2L$	heptane	13.7 ± 0.2	11.1	15.7	15.7	13.2	12.8	12.8	13.6	18.3	18.6	13.5	10.7	11.6	14.2	13.6	16.3
$(DMP)Mn(CO)_2L$	THF	22.1 ± 0.5	19.2	28.2	27.6	22.2	19.4	19.4	19.0	28.5	28.2	25.7	23.0	21.5	22.1	21.0	22.9
	η^2-benzene	14.9 ± 1.4	8.9	15.8	16.1	12.0	13.5	13.6	13.0	20.4	21.0	14.4	11.6	12.8	13.7	12.2	16.5
	bromohexane	21.1 ± 0.4	14.2	19.0	19.4	15.9	17.5	17.6	16.7	21.8	22.4	15.3	13.9	16.4	16.7	16.1	17.9
$TpRe(CO)_2L$	THF	23.9 ± 0.9	23.1	33.2	31.8	27.4	22.8	22.8	23.3	34.0	32.7	32.2	28.5	25.3	28.3	26.7	30.3
$CpRu(CO)(Cl)L$	η^2-cyclopentene	18.8 ± 1.1	13.3	20.5	20.7	19.2	17.9	18.1	20.0	27.6	28.2	22.4	20.8	18.5	18.4	17.5	21.8
	η^2-cyclohexene	17.2 ± 1.4	9.4	17.0	17.3	14.8	13.9	14.0	15.2	23.3	23.9	18.2	16.2	14.3	14.4	13.5	18.0
	η^2-cyclooctene	21.0 ± 0.6	13.3	21.1	21.3	19.3	17.9	18.0	19.7	27.9	28.5	22.0	20.4	18.3	18.7	17.7	22.1
	THF	13.7 ± 0.3	11.9	21.3	20.9	16.6	11.3	11.3	13.5	23.5	23.4	23.0	20.4	14.0	16.8	15.2	15.9
$(\mu\text{-}pdt)Fe_2(CO)_5L$	η^2-3-hexyne	20.9 ± 0.4	11.7	20.5	20.2	16.0	16.9	17.1	17.5	26.9	26.8	19.5	17.4	17.7	18.3	16.9	21.6
	η^2-cyclohexene	19.7 ± 0.6	10.0	19.0	17.7	14.9	15.1	15.3	16.3	25.8	24.8	18.2	16.1	16.1	16.7	15.1	19.9
	η^2-2,3-dihydrofuran	20.9 ± 1.6	12.0	19.6	18.5	16.7	17.2	17.4	17.6	25.7	24.8	18.4	16.8	17.5	17.9	16.5	20.2
		MUE	6.9	2.4	2.4	3.7	3.1	2.9	2.9	4.9	5.3	3.1	4.3	2.9	2.9	3.8	1.8
		MSE	-6.9	0.3	0.5	-3.2	-3.0	-2.9	-2.8	4.9	5.3	-0.8	-3.3	-2.7	-2.4	-3.5	0.1
		RMSD	7.6	3.3	3.1	4.3	3.6	3.4	3.5	5.5	5.8	4.1	5.1	3.4	3.6	4.4	2.3
		MAXD	13.6	9.3	7.9	9.3	7.3	7.1	7.0	10.1	9.7	9.3	10.3	7.3	8.0	9.7	6.4

Complex	Ligand L	Expt	Double Hybrids						Ab initio	
			B2PLYP	B2PLYPD	B2PLYP-GD3	B2PLYP-GD3BJ	MPW2PLYP	MPW2PLYPD	HF	MP2
$CpMn(CO)_2L$	η^2-2,3-dihydrofuran	28.4 ± 1.0	38.0	45.5	43.3	43.6	36.4	41.8	-13.6	59.5
	chloropropane	16.0 ± 0.6	20.7	23.8	23.9	24.4	20.4	22.7	-1.6	27.3
	η^2-cycloheptene	28.5 ± 0.8	35.0	43.4	41.0	41.3	33.4	39.6	-16.9	56.9
	η^2-cyclooctene	34.9 ± 0.7	39.3	47.3	45.1	45.4	37.6	43.5	-13.0	62.2
	η^2-furan	21.9 ± 1.0	28.1	34.5	32.6	33.2	26.8	31.5	-13.8	45.4
	$S(n\text{-}Bu)_2$	36.0 ± 1.0	40.3	45.9	45.6	46.6	39.2	43.3	1.7	53.4
	tetrahydrothiophene	37.0	41.3	45.8	45.6	46.7	40.0	43.3	2.1	53.6
	THF	24.0 ± 3.0	23.7	28.6	31.6	31.5	24.1	31.4	6.9	30.4
	thiophene	19.5	27.6	31.7	31.5	32.9	26.8	29.8	-3.0	38.3
	toluene	14.2 ± 0.8	18.4	26.0	24.1	24.8	17.8	23.3	-15.2	31.6
	TES	27.4 ± 0.8	37.0	45.1	43.5	44.8	35.1	40.9	-23.1	62.3
$BzCr(CO)_2L$	η^2-2,3-dihydrofuran	21.0 ± 1.0	24.9	32.5	30.0	30.8	24.6	30.1	-9.1	48.1
	η^2-3-hexyne	22.8 ± 0.4	24.2	31.9	30.0	31.5	24.2	29.7	-8.2	45.8
	η^2-benzene	11.5 ± 0.9	10.5	17.2	15.3	16.7	10.7	15.5	-9.8	23.2
	TES	24.3 ± 1.2	23.8	31.8	30.3	32.0	23.5	29.4	-12.0	48.0
	THF	21.4 ± 0.8	19.8	25.1	27.7	28.0	20.1	27.7	2.3	24.5
$Cr(CO)_5L$	η^2-benzene	11.4 ± 1.1	13.9	19.9	18.8	20.6	14.2	18.5	-4.8	28.4
	η^2-3-hexyne	18.3 ± 0.7	22.3	29.1	27.2	28.1	22.5	27.4	-7.4	43.4
$CpRe(CO)_2L$	heptane	13.7 ± 0.2	13.4	17.8	16.8	17.2	14.0	17.2	1.7	24.5
$(DMP)Mn(CO)_2L$	THF	22.1 ± 0.5	24.4	29.4	32.3	32.2	24.6	31.9	5.0	30.6
	η^2-benzene	14.9 ± 1.4	20.8	28.1	26.2	26.8	19.9	25.2	-13.7	31.9
	bromohexane	21.1 ± 0.4	22.6	26.2	26.2	27.0	22.0	24.6	-3.2	30.4
$TpRe(CO)_2L$	THF	23.9 ± 0.9	26.6	34.1	35.2	34.1	27.6	36.7	13.2	39.6
$CpRu(CO)(Cl)L$	η^2-cyclopentene	18.8 ± 1.1	18.9	27.1	24.5	25.4	19.7	25.7	-2.0	38.5
	η^2-cyclohexene	17.2 ± 1.4	14.8	23.0	20.8	21.6	15.6	21.5	-6.0	32.7
	η^2-cyclooctene	21.0 ± 0.6	19.0	27.2	25.0	25.8	19.8	25.8	-1.1	38.4
	THF	13.7 ± 0.3	12.4	18.0	20.7	20.9	13.7	21.4	6.8	19.7
$(\mu\text{-}pdt)Fe_2(CO)_5L$	η^2-3-hexyne	20.9 ± 0.4	26.9	34.8	33.7	33.6	26.3	32.0	-17.5	46.2
	η^2-cyclohexene	19.7 ± 0.6	24.0	32.8	30.9	30.1	23.4	29.8	-15.5	39.9
	η^2-2,3-dihydrofuran	20.9 ± 1.6	25.0	32.4	30.9	30.2	24.3	29.7	-12.2	39.2
		MUE	3.7	9.7	8.8	9.4	3.1	8.2	27.6	18.3
		MSE	3.0	9.7	8.8	9.4	2.7	8.2	-27.6	18.3
		RMSD	4.5	10.4	9.4	9.9	3.8	8.6	29.7	19.8
		MAXD	9.6	17.7	16.1	17.4	8.0	13.5	50.5	34.9

Table S9: Solvents used in the experimental study

Complex	Lignad	Solvent
$CpMn(CO)_2L$	η^2-2,3-dihydrofuran	cyclohexane
	chloropropane	dichloromethane
	η^2-cycloheptene	methylcyclohexane
	η^2-cyclooctene	methylcyclohexane
	η^2-furan	cyclohexane
	$S(n\text{-}Bu)_2$	methylcyclohexane
	tetrahydrothiophene	heptane
	THF	THF
	thiophene	heptane
	toluene	heptane
	TES	heptane
$BzCr(CO)_2L$	η^2-2,3-dihydrofuran	cyclohexane
	η^2-3-hexyne	heptane
	η^2-benzene	benzene
	TES	heptane
	THF	THF
$Cr(CO)_5L$	η^2-benzene	benzene
	η^2-3-hexyne	heptane
$CpRe(CO)_2L$	heptane	heptane
$(DMP)Mn(CO)_2L$	THF	cyclohexane
	η^2-benzene	cyclohexane
	bromohexane	cyclohexane
$TpRe(CO)_2L$	THF	THF
$CpRu(CO)(Cl)L$	η^2-cyclopentene	THF
	η^2-cyclohexene	THF
	η^2-cyclooctene	THF
	THF	THF
$(\mu\text{-pdt})Fe_2(CO)_5L$	η^2-3-hexyne	cyclohexane
	η^2-cyclohexene	cyclohexane
	η^2-2,3-dihydrofuran	cyclohexane

Table S10: Solvent corrected BDEs (kcal/mol) for the top twelve functionals from gas phase calculations.

Complex	Ligand L	Expt	Top 12 functionals											
			M06	M06L	ωB97XD	PW91 PW91	MPWB95	B3LYP-GD3	BLYP-GD3	PBEPBE	CAM-B3LYP-GD3	CAM-B3LYP-GD3BJ	B3LYP-GD3BJ	MN12L
$CpMn(CO)_2L$	η^2-2,3-dihydrofuran	28.4 ± 1.0	29.6	28.0	26.6	30.8	31.3	25.7	28.7	30.4	26.0	25.6	27.3	27.4
	chloropropane	16.0 ± 0.6	12.9	11.6	11.5	14.0	13.6	12.7	14.2	13.3	13.0	13.3	14.0	10.9
	η^2-cycloheptene	28.5 ± 0.8	25.8	24.8	24.4	26.7	27.6	23.2	26.2	26.3	23.2	22.9	24.7	24.5
	η^2-cyclooctene	34.9 ± 0.7	30.0	28.3	28.2	30.6	31.1	26.7	29.5	30.2	27.0	26.6	28.1	28.2
	η^2-furan	21.9 ± 1.0	21.0	19.1	18.5	22.0	22.0	18.0	20.4	21.5	18.1	18.2	20.0	18.7
	$S(n\text{-}Bu)_2$	36.0 ± 1.0	32.3	30.7	31.2	34.0	33.3	32.4	35.1	33.4	32.1	32.6	34.7	30.2
	tetrahydrothiophene	37.0	32.2	30.7	30.8	35.1	34.0	32.0	34.6	34.5	31.7	32.4	34.4	29.7
	THF	24.0 ± 3.0	22.9	21.9	22.9	20.3	20.3	23.7	24.3	19.5	24.9	24.3	23.9	21.6
	thiophene	19.5	20.6	18.5	19.4	22.0	21.0	20.4	22.2	21.4	20.4	21.5	23.2	18.0
	toluene	14.2 ± 0.8	14.0	12.8	12.4	13.0	13.5	12.3	14.9	12.4	11.8	12.0	14.1	12.4
	TES	27.4 ± 0.8	25.9	24.4	26.2	28.8	29.9	24.1	27.6	28.7	24.1	24.8	27.2	25.9
$BzCr(CO)_2L$	η^2-2,3-dihydrofuran	21.0 ± 1.0	23.3	22.0	20.8	22.8	24.0	19.7	21.6	22.3	20.0	20.2	22.3	20.7
	η^2-3-hexyne	22.8 ± 0.4	21.7	20.4	21.8	21.9	22.5	20.1	22.6	21.2	19.9	21.0	23.6	18.7
	η^2-benzene	11.5 ± 0.9	8.7	8.7	8.4	6.6	7.6	7.8	9.2	6.0	7.3	8.5	10.9	8.8
	TES	24.3 ± 1.2	21.9	20.1	22.5	21.8	23.2	20.1	22.2	21.4	20.2	21.5	24.0	21.1
	THF	21.4 ± 0.8	19.6	19.6	19.3	17.2	17.8	19.7	20.5	16.4	20.6	20.5	20.9	18.8
$Cr(CO)_5L$	η^2-benzene	11.4 ± 1.1	12.2	12.3	12.4	10.1	11.1	12.2	12.8	9.4	12.1	13.5	16.1	12.8
	η^2-3-hexyne	18.3 ± 0.7	19.7	18.6	19.5	18.8	19.8	17.1	17.8	18.2	18.2	18.8	19.5	17.7
$CpRe(CO)_2L$	heptane	13.7 ± 0.2	9.8	7.7	12.2	9.1	8.2	10.4	9.8	8.5	11.6	11.6	11.3	8.4
$(DMP)Mn(CO)_2L$	THF	22.1 ± 0.5	25.0	24.7	25.2	24.0	23.8	26.4	27.6	23.2	27.3	26.8	26.7	24.1
	η^2-benzene	14.9 ± 1.4	15.4	15.2	14.4	16.7	17.5	14.5	17.9	16.1	13.8	14.0	16.3	14.0
	bromohexane	21.1 ± 0.4	17.7	16.5	15.8	19.3	19.0	17.1	19.3	18.8	16.8	17.3	18.7	15.2
$TpRe(CO)_2L$	THF	23.9 ± 0.9	20.0	18.7	22.3	14.7	14.8	20.1	19.6	13.8	21.9	20.4	18.4	17.9
$CpRu(CO)(Cl)L$	η^2-cyclopentene	18.8 ± 1.1	18.9	17.2	20.7	16.7	16.9	17.7	16.1	16.1	19.6	19.8	20.2	24.1
	η^2-cyclohexene	17.2 ± 1.4	14.2	12.6	16.1	12.4	12.3	13.9	13.0	11.7	15.2	15.4	16.3	18.8
	η^2-cyclooctene	21.0 ± 0.6	18.5	16.5	20.4	15.8	15.6	17.6	16.1	15.2	19.3	19.5	20.0	22.8
	THF	13.7 ± 0.3	15.7	16.7	17.6	12.2	12.5	17.3	15.9	11.4	19.6	19.2	18.3	22.4
$(\mu\text{-}pdt)Fe_2(CO)_5L$	η^2-3-hexyne	20.9 ± 0.4	20.2	19.2	20.2	18.2	18.9	18.7	19.6	17.6	19.1	18.8	19.5	21.3
	η^2-cyclohexene	19.7 ± 0.6	20.8	19.8	19.3	16.8	18.0	17.9	18.4	16.2	18.4	17.1	17.3	21.7
	η^2-2,3-dihydrofuran	20.9 ± 1.6	22.0	21.4	19.6	19.6	20.6	18.7	19.7	19.0	19.1	18.0	18.4	23.0
		MUE	2.1	2.8	2.3	2.6	2.5	2.9	2.1	3.0	2.8	2.7	2.1	3.2
		MSE	-1.1	-2.3	-1.5	-1.8	-1.5	-2.3	-1.0	-2.4	-1.8	-1.7	-0.5	-1.6
		RMSD	2.5	3.4	2.9	3.2	3.2	3.3	2.6	3.6	3.3	3.2	2.7	3.9
		MAXD	4.9	6.6	6.7	9.2	9.1	8.2	5.5	10.1	7.9	8.3	6.8	8.7

M06 level Optimized Geometries of all complexes used in the present benchmark study

(A) $CpMn(CO)_2L$

1. 2,3, dihydrofuran (DHF)

C	2.0162890	-1.2398300	-0.7318260
C	1.7713650	-0.1739430	-1.6233500
C	2.0623170	1.0431020	-0.9681150
C	2.4684020	-0.6753990	0.4923340
C	2.4970800	0.7235150	0.3459270
H	1.8854110	-2.2896970	-0.9386830
H	1.3913330	-0.2707320	-2.6295140
H	1.9710800	2.0323390	-1.3862920
H	2.7282520	-1.2230750	1.3839260
H	2.7809730	1.4316050	1.1078780
C	-0.1691030	-1.1473880	1.2606200
O	-0.5354170	-1.9174630	2.0261170
C	-0.1267580	1.3920760	1.0562340
O	-0.4967010	2.2833960	1.6785220
Mn	0.4907020	0.0287430	0.0830250
C	-1.1468220	-0.7821970	-1.1526040
C	-1.1126820	0.6008330	-1.2523240
C	-2.4552530	1.0864680	-0.7609620
C	-2.9571420	-0.1314110	0.0028760
O	-2.2924550	-1.2526490	-0.5803920
H	-0.6596840	-1.5074700	-1.7887190
H	-0.6144440	1.1185990	-2.0590440
H	-3.0915460	1.3006930	-1.6255550
H	-4.0299560	-0.3024260	-0.0687010
H	-2.6873270	-0.0715370	1.0633870
H	-2.4311990	1.9819060	-0.1411400

2. Chloropropane

C	0.9279600	-1.9165310	0.8156720
C	0.7613580	-1.9885320	-0.5811120
C	1.8728940	-1.3921660	-1.2137600
C	2.1704310	-1.2603780	1.0613330
C	2.7492490	-0.9419690	-0.1846340
H	0.2502220	-2.2979470	1.5621410
H	-0.1057850	-2.3836440	-1.0892860
H	2.0351130	-1.3070220	-2.2753470
H	2.5958540	-1.0494910	2.0291620
H	3.6925660	-0.4407070	-0.3315370
C	0.4766860	0.9153090	1.5455540
O	0.2397970	1.4041620	2.5593260
C	1.6724550	1.5654240	-0.6532750
O	2.2327590	2.4771290	-1.0685830
Mn	0.9200880	0.0803090	0.0234270
C	-2.4699910	-0.0714810	0.0854680
H	-2.2235580	-1.1068030	0.3216270
H	-2.3587500	0.5316760	0.9859470
C	-3.8242690	0.0754250	-0.5514880
H	-3.9823520	1.1210630	-0.8251030
H	-3.8527030	-0.4988470	-1.4804190
C	-4.9092800	-0.3951840	0.3990230
H	-4.9032200	0.1847110	1.3235420
H	-5.8963810	-0.2931060	-0.0498910
H	-4.7732560	-1.4447220	0.6662960
Cl	-1.1661980	0.4933690	-1.0403190

3. Cycloheptene

C	-2.4256880	0.7351820	-1.3077960
C	-2.0705720	-0.5809790	-1.6684340
C	-2.3810170	-1.4474130	-0.5986020
C	-2.9684970	0.6832520	0.0047470
C	-2.9418540	-0.6553650	0.4385740
H	-2.3069130	1.6184010	-1.9142050
H	-1.6029630	-0.8727300	-2.5967840
H	-2.2215490	-2.5130130	-0.5720270
H	-3.3253270	1.5251270	0.5762730
H	-3.2740570	-1.0138140	1.3997990
C	-0.4728500	1.5883890	0.7497140
O	-0.2512830	2.6275230	1.1855050
C	-0.4358710	-0.8069780	1.5762190
O	-0.1806440	-1.3364700	2.5625260
Mn	-0.9435220	0.0065370	0.0717550
C	1.8783620	1.3744580	-0.9589910
C	0.8146540	0.3421420	-1.2249920
C	0.8288580	-0.9764160	-0.7946850
C	2.7436490	1.1580430	0.2714230
C	1.9479190	-1.6241360	-0.0016110
C	3.8176510	0.0929060	0.0947110
C	3.3253170	-1.2156970	-0.5164810
H	2.5286490	1.3977910	-1.8455220
H	0.3075270	-1.6843920	-1.4304240
H	1.9007320	-1.4102880	1.0674360
H	2.1073060	0.9085000	1.1252320
H	4.2601660	-0.1142940	1.0736790
H	1.4183120	2.3649330	-0.9226750
H	0.2740000	0.5452710	-2.1445530
H	3.2264300	2.1007590	0.5386110
H	1.8248750	-2.7060020	-0.0812410
H	4.6265320	0.4936570	-0.5243340
H	4.0525400	-2.0027110	-0.3028640
H	3.2868570	-1.1333690	-1.6072950

4. Cyclooctene

C	2.2165100	-1.7262320	-0.7154420
C	2.0911050	-0.7616560	-1.7481190
C	2.7929300	0.3946860	-1.3674440
C	3.0075900	-1.1545220	0.3068560
C	3.3560700	0.1549750	-0.0805680
H	1.7880630	-2.7152720	-0.7094540
H	1.5244760	-0.8826000	-2.6588370
H	2.8793900	1.3049020	-1.9386360
H	3.2728520	-1.6273380	1.2391900
H	3.9469850	0.8499720	0.4936100
C	0.7472890	-0.4065610	1.7238060
O	0.5058660	-0.7056690	2.8055140
C	-4.1769500	-0.8301810	0.0150650
C	-3.9299460	0.6582350	0.2420660
C	-0.6711340	-0.8127490	-0.5457090
C	-3.0588870	1.4042300	-0.7732180
C	-0.6570470	0.5206660	-0.9323900
C	-1.5830060	1.5619070	-0.3630860
H	-4.9349580	-0.9497580	-0.7656150
H	-3.5020050	0.8112370	1.2379190
H	-3.1275820	0.9326610	-1.7599200
H	-0.3570990	-1.5323840	-1.2967700
H	-0.3259480	0.7373270	-1.9451820
H	-4.6309550	-1.2286140	0.9278680
H	-4.9119100	1.1366450	0.2855320
H	-3.4732120	2.4067830	-0.9001290
H	-1.2293920	2.5446880	-0.6809920
H	-1.5290610	1.5729040	0.7297660
C	-2.9795570	-1.6942000	-0.3662160

H	-2.7821360	-1.5756340	-1.4364040
H	-3.2640540	-2.7416790	-0.2427910
C	-1.6764520	-1.4037320	0.4003850
H	-1.8720780	-0.7406050	1.2454780
H	-1.2742240	-2.3228560	0.8323940
C	1.1357440	1.7627970	0.4695380
O	1.1500000	2.8810160	0.7255420
Mn	1.2348150	0.0244350	0.0600560

5. furan

C	1.8431640	-1.5391300	-0.3261490
C	1.7184930	-0.7282070	-1.4799370
C	2.1311850	0.5804120	-1.1634840
C	2.3395190	-0.7153010	0.7163110
C	2.5125260	0.5868980	0.2088130
H	1.6105250	-2.5890530	-0.2525430
H	1.3394880	-1.0507280	-2.4386760
H	2.1516660	1.4242320	-1.8340330
H	2.5321010	-1.0269750	1.7304950
H	2.8678210	1.4400320	0.7638650
C	-0.2922260	-0.5003420	1.6022360
O	-0.7204670	-0.8671390	2.5998770
C	-0.0271310	1.7458280	0.4162030
O	-0.2894090	2.8410160	0.6332740
Mn	0.4577860	0.0531750	0.0706100
C	-1.1973480	-1.0563980	-0.8987050
C	-1.2596100	0.2501020	-1.3795000
C	-2.5039650	0.7792520	-0.8680030
C	-3.0720950	-0.2065780	-0.1587050
O	-2.3373110	-1.3417730	-0.1849390
H	-0.7220500	-1.9278300	-1.3180730
H	-0.7397310	0.6342470	-2.2423690
H	-3.9759510	-0.2465240	0.4268010
H	-2.8860810	1.7771670	-1.0008880

6. S(*n*-But)$_2$

C	-2.6825080	1.5544710	0.0483050
C	-2.1971160	1.2864940	-1.2467480
C	-2.7512490	0.0665530	-1.7016670
C	-3.5528290	0.4863360	0.4119220
C	-3.5937520	-0.4225930	-0.6656150
H	-2.4419650	2.4128820	0.6548650
H	-1.4909830	1.8963870	-1.7923880
H	-2.5762190	-0.3970590	-2.6582240
H	-4.0873440	0.3923080	1.3429520
H	-4.1610080	-1.3392260	-0.6941200
C	-1.1154640	-0.2106790	1.7896430
O	-0.8132460	-0.1226960	2.8977230
C	-1.4962410	-2.0906450	0.0697780
O	-1.4771010	-3.2415780	0.0582070
Mn	-1.6147320	-0.3063950	0.0779610
S	0.5212950	-0.0072600	-0.7046790
C	1.6079060	-1.2733820	0.0190270
H	1.4369480	-1.2832080	1.0999410
H	1.2125520	-2.2078810	-0.3818810
C	3.0770640	-1.1145630	-0.3060150
H	3.4391660	-0.1594610	0.0859370
H	3.2075240	-1.0765250	-1.3932270
C	3.9239590	-2.2389180	0.2751660
H	4.9771120	-1.9990780	0.1082140
H	3.7900490	-2.2649450	1.3615850
C	3.6174680	-3.6018590	-0.3145650
H	4.3127460	-4.3574410	0.0509120
H	2.6121940	-3.9421770	-0.0619380
H	3.6936880	-3.5812240	-1.4043790
C	1.1957400	1.4911640	0.0970760
H	1.6694720	1.1818050	1.0344370
H	0.3226720	2.0859880	0.3660270
C	2.1424900	2.2682260	-0.7962880
H	2.8736810	1.5877480	-1.2394970
H	1.5728100	2.6832950	-1.6356840
C	2.8655840	3.3846090	-0.0595590
H	3.4741360	2.9467900	0.7398350
H	3.5696360	3.8587570	-0.7480480
C	1.9367940	4.4344510	0.5191610
H	1.2767540	4.8384500	-0.2526620
H	1.3059810	4.0279250	1.3114280
H	2.4936740	5.2681370	0.9466000

7. tetrahydrothiophene

C	1.8460500	-1.7472950	0.5283680
C	1.4585630	-1.7707270	-0.8268820
C	2.1161110	-0.7235130	-1.5117760
C	2.7634470	-0.6691630	0.6928880
C	2.9267080	-0.0435020	-0.5601940
H	1.5124800	-2.4238490	1.2984180
H	0.7486450	-2.4569550	-1.2650150
H	2.0288680	-0.4926060	-2.5604490
H	3.2467530	-0.3828710	1.6126950
H	3.5553490	0.8091290	-0.7611260
C	0.3595750	0.5021140	1.7009900
O	0.0296610	0.7247590	2.7820030
C	0.8576800	1.8422990	-0.4393150
O	0.8679720	2.9484140	-0.7545090
Mn	0.9062080	0.1190620	0.0464850
C	-2.3636050	1.0634150	-0.3099300
C	-3.7374580	0.4106350	-0.3481970
C	-3.5963290	-1.0798990	0.0284290
C	-2.1394830	-1.3637210	0.3549810
S	-1.1934210	-0.2582510	-0.7397140
H	-2.2416410	1.8851050	-1.0130850
H	-4.1595170	0.5001560	-1.3492110
H	-3.9105310	-1.7029760	-0.8093570
H	-1.8346260	-2.3926670	0.1692130
H	-1.8855490	-1.1050270	1.3849760
H	-2.1021460	1.4201250	0.6885590
H	-4.4156260	0.9333620	0.3271030
H	-4.2315400	-1.3446950	0.8744430

8. THF

C	1.2626080	-1.8301390	0.7902750
C	0.5092020	-2.0045140	-0.3866190
C	1.1738190	-1.3811400	-1.4636100
C	2.4247600	-1.0789000	0.4408130
C	2.3700900	-0.8057970	-0.9409730
H	1.0163750	-2.2055150	1.7703110
H	-0.4581270	-2.4846070	-0.4426960
H	0.8512250	-1.3615920	-2.4918270
H	3.2108500	-0.7787330	1.1147020
H	3.1072150	-0.2580820	-1.5059720
C	0.9424180	1.0323170	1.5427840
O	1.1547080	1.5890160	2.5269720
C	-2.1415090	0.2669480	-1.1357670
O	-1.3540110	0.2208330	0.0522310
C	-2.1345470	-0.2308640	1.1628710
C	-3.4632620	-0.6512630	0.5709280
C	-3.5705150	0.2550660	-0.6468090
H	-1.8571290	1.1595310	-1.6936590
H	-1.9172290	-0.6125160	-1.7526640
H	-1.5975870	-1.0399750	1.6608650
H	-2.2339530	0.5997830	1.8686580
H	-3.4233510	-1.6971750	0.2558730
H	-4.2873430	-0.5413940	1.2733050
H	-4.2681040	-0.1081380	-1.3992310
H	-3.8781120	1.2598050	-0.3498390
C	0.9363090	1.5800960	-0.9805170
O	1.1419640	2.4957230	-1.6466090
Mn	0.7335100	0.1085270	0.0204470

9. thiophene

C	1.6974560	-1.7334460	0.5734870
C	1.4988310	-1.6983660	-0.8215920
C	2.2004470	-0.5957590	-1.3611770
C	2.5382220	-0.6341070	0.9131840
C	2.8452920	0.0607020	-0.2761690
H	1.2890420	-2.4590370	1.2580300
H	0.8839750	-2.3853930	-1.3849940
H	2.2504350	-0.3159960	-2.4002990
H	2.8819940	-0.3804580	1.9026780
H	3.4612460	0.9427870	-0.3483500
C	-0.0114070	0.3976160	1.6566110
O	-0.4666510	0.5476450	2.6993930
C	0.7374260	1.8761330	-0.3309670
O	0.7764040	2.9980530	-0.5773420
Mn	0.7638450	0.1246860	0.0585630
C	-2.4547110	0.9151750	-0.6737290
C	-3.5067130	0.3866420	-0.0171490
C	-3.3437250	-1.0048970	0.2696660
C	-2.1700190	-1.4965760	-0.1752020
S	-1.2495710	-0.2822160	-0.9983660
H	-2.2968770	1.9295820	-1.0042480
H	-4.3799060	0.9566640	0.2673590
H	-4.0811480	-1.5967390	0.7935260
H	-1.7763730	-2.4973780	-0.0920900

10. toulene

C	1.7930900	-1.7312520	-0.5737910
C	1.8922550	-0.7492450	-1.5892900
C	2.5687840	0.3726820	-1.0802270
C	2.4191500	-1.1994410	0.5835440
C	2.8900110	0.0948750	0.2804210
H	1.3390660	-2.7048740	-0.6654830
H	1.4845580	-0.8324430	-2.5860810
H	2.7974160	1.2788820	-1.6172650
H	2.5080480	-1.6936100	1.5379920
H	3.4083010	0.7544230	0.9575540
C	-0.0666760	-0.5229540	1.5519700
O	-0.5429320	-0.9185420	2.5189070
C	0.6931000	1.7494120	0.6632220
O	0.7147300	2.8292940	1.0505560
Mn	0.7862140	0.0526670	0.0846640
C	-1.1697380	-0.5263740	-1.1357710
C	-0.9264910	0.8171960	-1.4247060
C	-1.8041990	1.8012310	-0.9150730
C	-2.8606910	1.4334190	-0.1347650
C	-3.1012910	0.0772210	0.1525380
C	-2.2856280	-0.9024840	-0.3424990
H	-0.6735490	-1.3063920	-1.6987330
H	-0.2167100	1.0929170	-2.1933960
H	-1.6302710	2.8431890	-1.1511390
H	-3.5314700	2.1874600	0.2570890
H	-3.9516590	-0.1975870	0.7657790
C	-2.5178730	-2.3504240	-0.0771430
H	-1.6603980	-2.7889920	0.4415680
H	-3.4020360	-2.5116400	0.5380920
H	-2.6438490	-2.9072050	-1.0088730

11. triethyl silane (TES)

C	-1.6153000	-1.2243250	-1.7104790
C	-1.0015180	-1.9788980	-0.6749800
C	-1.8413270	-1.9187580	0.4607440
C	-2.8243930	-0.7056270	-1.2090820
C	-2.9704870	-1.1247230	0.1373010
H	-1.2146450	-1.0617130	-2.6978710
H	-0.0823110	-2.5359370	-0.7561740
H	-1.6463860	-2.3844900	1.4140690
H	-3.5074270	-0.0684630	-1.7481530
H	-3.7922990	-0.8878870	0.7923340
C	-1.8295450	1.7116890	-0.2327140
O	-2.2514480	2.7654420	-0.3786090
C	-0.8609640	0.4339330	1.6755560
O	-0.7095010	0.6692120	2.7902710
Mn	-1.2014670	0.0419690	-0.0288250
Si	1.2665150	-0.0032160	0.0171060
H	-0.0695140	0.7075170	-0.8756750
C	1.7262090	-1.2621380	1.3630070
H	1.4451940	-0.8263340	2.3256640
H	1.1104240	-2.1589950	1.2525030
C	3.1986500	-1.6523120	1.3871380
H	3.4207380	-2.3265840	2.2168480
H	3.4965710	-2.1633410	0.4694920
H	3.8480150	-0.7814130	1.5000920
C	2.0426530	-0.5844490	-1.6213210
H	1.4426760	-0.1861080	-2.4451440
H	1.9341660	-1.6736220	-1.6795610
C	3.5038780	-0.2045880	-1.8310020
H	4.1474700	-0.5895670	-1.0386560
H	3.8887090	-0.5923740	-2.7764270
H	3.6366230	0.8786690	-1.8507120
C	2.0435470	1.6369800	0.5195470
H	1.6998660	1.8834730	1.5290770
H	3.1227380	1.4706380	0.6085130
C	1.7682730	2.7930510	-0.4300630
H	2.3196200	3.6934810	-0.1534880
H	2.0457570	2.5471750	-1.4588460
H	0.7090240	3.0554310	-0.4419650

(B) $BzCr(CO)_2L$

12. 2,3-dihydrofuran

C	-0.2963410	-1.0432730	1.3714810
O	-0.7264160	-1.7195400	2.1954130
C	-0.2485120	1.4649160	0.9974250
O	-0.6808010	2.3609300	1.5775250
C	-1.3027040	-0.8728470	-1.1189000
C	-1.2451490	0.4931950	-1.3239250
C	-2.5653040	1.0414730	-0.8361030
C	-3.0671370	-0.1042780	0.0326650
O	-2.4295580	-1.2795480	-0.4735730
H	-0.8369850	-1.6554960	-1.6993340
H	-0.7678830	0.9307710	-2.1879930
H	-3.2230810	1.2029700	-1.6965950
H	-4.1433230	-0.2656490	-0.0049100
H	-2.7730420	0.0335390	1.0784230
H	-2.5079280	1.9794070	-0.2855040
Cr	0.4642500	0.0349070	0.0793080
C	1.8712640	0.9699370	-1.3450480
C	2.2895530	1.2283230	-0.0342980
C	2.4908230	0.1759160	0.8781730
C	2.2544970	-1.1451000	0.4631320
C	1.8347140	-1.4230590	-0.8478780
C	1.6081850	-0.3570390	-1.7325620
H	1.6758350	1.7865240	-2.0255800
H	2.4165140	2.2511350	0.2945880
H	2.7817550	0.3838650	1.8971340
H	2.3547950	-1.9533690	1.1751790
H	1.6181980	-2.4388590	-1.1470960
H	1.2140080	-0.5563450	-2.7215900

13. 3-hexyne

C	-0.7714660	0.8307100	1.5948790
O	-0.9867730	1.5322980	2.4824470
C	0.4374140	-1.3759630	1.3471950
O	0.9879590	-2.0811300	2.0721090
Cr	-0.4679090	-0.2909230	0.1604760
C	1.5782380	0.1462450	-0.5521380
C	1.1349250	1.2475450	-0.2070700

C	1.1313360	2.6898750	0.0670760
H	1.0562910	2.8485590	1.1467110
H	2.1037320	3.0935460	-0.2337360
C	0.0214280	3.4574460	-0.6300670
H	-0.9577380	3.1051540	-0.3025730
H	0.0882260	4.5219580	-0.4062800
H	0.0804390	3.3367980	-1.7130890
C	2.5981000	-0.8193480	-0.9948800
H	2.8737970	-0.5939860	-2.0307160
H	2.1897700	-1.8330800	-1.0030940
C	3.8333610	-0.7732420	-0.1067540
H	3.5722350	-1.0168500	0.9233750
H	4.5859160	-1.4858030	-0.4458290
H	4.2768710	0.2226100	-0.1116990
C	-1.3721790	0.3238990	-1.7546460
C	-0.6674990	-0.8788430	-1.9481620
C	-0.9199810	-1.9883460	-1.1341380
C	-1.9018750	-1.9059890	-0.1191430
C	-2.6122940	-0.7195120	0.0653630
C	-2.3327600	0.4059070	-0.7412700
H	-1.1278840	1.1955750	-2.3452230
H	0.1168550	-0.9262210	-2.6917650
H	-0.3385950	-2.8925760	-1.2520000
H	-2.0759130	-2.7477660	0.5365520
H	-3.3227950	-0.6391730	0.8763750
H	-2.8413590	1.3417570	-0.5523560

14. benzene

C	-0.1087680	-0.7848300	1.5751680
O	-0.5184960	-1.2951090	2.5204770
C	0.0436370	1.6519060	0.7740280
O	-0.2642030	2.6660230	1.2208870
Cr	0.6525820	0.0354080	0.0912390
C	-1.4382380	0.3881230	-1.4813780
C	-2.4290020	1.1893100	-0.8941110
C	-3.3575550	0.6350830	-0.0506860
C	-3.3332980	-0.7376690	0.2178200
C	-2.3790420	-1.5348260	-0.3605880
C	-1.4149240	-0.9782000	-1.2136880
H	-0.7930320	0.8117540	-2.2387780
H	-2.4522730	2.2500480	-1.1092720
H	-4.1170870	1.2592400	0.4022080
H	-4.0728010	-1.1708150	0.8789130
H	-2.3649860	-2.5993630	-0.1640430
H	-0.7589270	-1.6339350	-1.7674670
C	2.3086120	-1.3095550	0.4205310
C	1.8362850	-1.5351210	-0.8843680
C	1.7106580	-0.4399130	-1.7631960
C	2.0709220	0.8524320	-1.3694650
C	2.5218860	1.0599030	-0.0436600
C	2.6850670	-0.0206090	0.8379540
H	2.3498130	-2.1312350	1.1231730
H	1.5314990	-2.5251130	-1.1916220
H	1.2883920	-0.5959950	-2.7488690
H	1.9420600	1.6886040	-2.0416380
H	2.7361210	2.0637060	0.2977520
H	3.0133980	0.1498150	1.8528440

15. TES

C	-1.5307480	1.9157290	-0.1251010
O	-1.7641810	3.0376840	-0.1950090
C	-0.6016300	0.4530010	1.6998480
O	-0.2609640	0.6612380	2.7823280
Si	1.3965860	-0.0565440	-0.1341610
H	0.0812290	0.5352070	-0.9488430
C	1.8479190	-1.4200130	1.1225850
H	1.0047800	-1.6324920	1.7804720
H	2.0164680	-2.3335280	0.5400400
C	3.0760220	-1.1098060	1.9692740
H	3.3272580	-1.9417180	2.6304950
H	3.9570260	-0.9045350	1.3573970
H	2.9070230	-0.2341260	2.5987100
C	2.1406900	-0.6392210	-1.7780350
H	1.8904610	0.0926270	-2.5527370
H	1.6371370	-1.5667540	-2.0739930
C	3.6452120	-0.8638390	-1.7275910
H	3.9134840	-1.6238180	-0.9900400
H	4.0458980	-1.1939140	-2.6881090
H	4.1770480	0.0505700	-1.4537690
C	2.2181230	1.5722880	0.3310560
H	1.7761940	1.9407560	1.2612040
H	3.2698200	1.3753190	0.5612200
C	2.1166690	2.6292570	-0.7597210
H	2.5689380	3.5744510	-0.4545680
H	2.6229150	2.3102770	-1.6738700
H	1.0782050	2.8401740	-1.0234640
Cr	-1.1898790	0.0962200	-0.0031420
C	-1.5609190	-1.2163260	-1.7218630
C	-1.0904560	-1.9843860	-0.6335240
C	-1.7541230	-1.9111060	0.6011520
C	-2.8778410	-1.0738740	0.7573240
C	-3.3066750	-0.2811390	-0.3088570
C	-2.6547710	-0.3658790	-1.5642300
H	-1.0222270	-1.2299810	-2.6597120
H	-0.2276180	-2.6253970	-0.7488080
H	-1.3767660	-2.4686610	1.4475070
H	-3.3530760	-0.9834240	1.7238270
H	-4.1245560	0.4120110	-0.1720940
H	-2.9684130	0.2697980	-2.3796760

16. THF

C	-0.5794460	1.9074150	-0.3646960
O	-0.5899460	3.0348110	-0.6094210
C	2.1377420	-1.3379870	0.1140730
O	1.4024860	-0.2917030	-0.5371540
C	2.2764900	0.8121430	-0.8057800
C	3.6709930	0.2463610	-0.6974710
C	3.4890480	-0.7444720	0.4415510
H	1.5748340	-1.6633400	0.9899760
H	2.2247040	-2.1801600	-0.5809340
H	2.0152210	1.2161130	-1.7840080
H	2.1071440	1.5889150	-0.0519630
H	3.9529100	-0.2722970	-1.6168180
H	4.4156340	1.0138110	-0.4940780
H	4.2730540	-1.4970680	0.5041300
H	3.4440010	-0.2137910	1.3959740
Cr	-0.6786300	0.1036320	0.0392870
C	-0.1161190	0.5204810	1.7562180
O	0.1896970	0.7729030	2.8397330
C	-1.5238730	-1.8444330	0.5838420
C	-2.3766490	-0.7693490	0.9572740
C	-2.8420210	0.1347230	-0.0135250
C	-2.3584880	0.0419620	-1.3317020
C	-1.4511560	-0.9644040	-1.6968240
C	-1.0540480	-1.9140400	-0.7249470
H	-1.1787770	-2.5497790	1.3271930
H	-2.6936540	-0.6642920	1.9855220
H	-3.4949520	0.9475040	0.2700300
H	-2.6381240	0.7958860	-2.0557700
H	-1.0438920	-0.9988280	-2.6964820
H	-0.3237310	-2.6683450	-0.9890000

(C) $Cr(CO)_5L$

17. benzene

Cr	0.7227380	0.0000580	0.0309140
C	0.7528100	1.9127580	0.0687340
C	0.7530200	-1.9126390	0.0687000
C	1.6582710	0.0001260	-1.6370840

C	2.3399500	0.0000910	0.9237120
C	-0.2161730	0.0000200	1.7020620
O	0.7996910	3.0504490	0.1173330
O	0.8000400	-3.0503260	0.1173090
O	2.2457930	-0.0000280	-2.6137640
O	3.3429780	0.0000120	1.4755250
O	-0.7349800	0.0000630	2.7152790
C	-3.2744590	-0.6987690	0.2906140
C	-2.3983610	-1.3897320	-0.5106200
C	-1.5046430	-0.6958830	-1.3366470
C	-1.5049990	0.6961880	-1.3365680
C	-2.3990710	1.3895000	-0.5104830
C	-3.2748200	0.6980030	0.2906760
H	-3.9683240	-1.2369060	0.9233540
H	-2.4006390	-2.4725180	-0.5191790
H	-0.9113040	-1.2375020	-2.0614240
H	-0.9118720	1.2381880	-2.0612370
H	-2.4019210	2.4722860	-0.5189440
H	-3.9689740	1.2357220	0.9234560

18. 3-hexyne

Cr	-0.6174140	-0.0009020	-0.0269460
C	-1.1808530	-0.0027020	1.8055040
C	0.1476700	0.0010990	-1.7871230
C	-0.8089990	-1.8929720	-0.0596620
C	-2.3626490	-0.0033360	-0.6777800
C	-0.8149990	1.8905870	-0.0576760
O	-1.5083500	-0.0039340	2.8954200
O	0.6304090	0.0020880	-2.8180470
O	-1.0084530	-3.0160020	-0.0838190
O	-3.4334420	-0.0046590	-1.0795990
O	-1.0181770	3.0129730	-0.0806870
C	1.5326660	-0.6105640	0.7486900
C	1.5309350	0.6149660	0.7486960
C	2.0313670	1.9882890	0.8680060
H	2.9048370	1.9519220	1.5263080
H	1.3026860	2.6281880	1.3696360
C	2.4289720	2.5892200	-0.4722000
H	1.5715250	2.6881410	-1.1372810
H	2.8595790	3.5801820	-0.3335100
H	3.1665310	1.9612780	-0.9726580
C	2.0370080	-1.9824540	0.8680600
H	2.9098040	-1.9437630	1.5271210
H	1.3097720	-2.6246520	1.3688470
C	2.4375170	-2.5817270	-0.4720290
H	2.8706740	-3.5715830	-0.3333740
H	1.5809750	-2.6826600	-1.1379730
H	3.1738500	-1.9515620	-0.9714940

(D) $CpRe(CO)_2L$

19. heptane

C	1.6132980	1.9823320	-1.1397990
C	0.5690510	2.0464150	-0.1887350
C	1.1055010	1.9186370	1.1135340
C	2.8300320	1.7668520	-0.4173670
C	2.5166130	1.7289030	0.9711560
H	1.5141770	2.0893450	-2.2071790
H	-0.4806510	2.1584510	-0.4210690
H	0.5559470	1.9677980	2.0388330
H	3.8182440	1.7035560	-0.8425400
H	3.2275410	1.6299080	1.7751730
C	2.6213510	-1.1504860	-1.1969380
O	3.3089690	-1.7276040	-1.9215740
C	2.0667650	-1.2058070	1.4318570
O	2.4136940	-1.8131980	2.3504730
Re	1.6023460	-0.0454390	-0.0129360
C	-0.7224190	-1.1335190	-0.7041650
H	-0.5815960	-0.3214440	-1.4171280
H	0.1901770	-1.4265790	-0.0971690
H	-0.8668450	-2.0363020	-1.3013880
C	-1.8844250	-0.8703840	0.2293030
H	-2.0218280	-1.7235770	0.9008600
H	-1.6519270	-0.0176910	0.8761040
C	-3.1708810	-0.5998520	-0.5258750
H	-3.3876040	-1.4418420	-1.1944440
H	-3.0303670	0.2700730	-1.1807400
C	-4.3577310	-0.3594530	0.3850060
H	-4.1366340	0.4780500	1.0580120
H	-4.4998740	-1.2317600	1.0342060
C	-5.6422990	-0.0762370	-0.3668700
H	-5.8624200	-0.9130570	-1.0411810
H	-5.5011130	0.7972960	-1.0154660
C	-6.8313570	0.1612620	0.5433310
H	-6.6072140	0.9955980	1.2165850
H	-6.9695090	-0.7128320	1.1885570
C	-8.1060820	0.4441010	-0.2238430
H	-8.3598320	-0.3903120	-0.8814240
H	-8.9548170	0.6125640	0.4392850
H	-7.9956370	1.3305250	-0.8524800

(E) (DMP)$Mn(CO)_2L$

20. THF

C	1.9086770	-1.1001700	-0.8173370
C	0.9192030	-0.7124060	-1.7371990
C	0.9192180	0.7123310	-1.7372000
C	1.9086980	1.1000800	-0.8173470
N	2.4960160	-0.0000510	-0.2396970
H	0.2954430	-1.3703720	-2.3225140
H	0.2954640	1.3703030	-2.3225160
C	2.3824880	2.4703910	-0.5030020
H	2.7216340	2.5310600	0.5302640
H	3.2255630	2.7340520	-1.1448760
H	1.5949440	3.2079720	-0.6593940
C	2.3823800	-2.4705030	-0.5029460
H	2.7215140	-2.5311550	0.5303250
H	1.5947750	-3.2080280	-0.6593070
H	3.2254360	-2.7342640	-1.1448040
Mn	0.4108550	-0.0000490	0.2214790
C	0.2783150	-1.2815030	1.4732810
C	0.2785100	1.2815540	1.4731490
O	0.2725610	-2.1130400	2.2673400
O	0.2729660	2.1132080	2.2670850
C	-2.4430780	1.1334070	-0.0677700
O	-1.6170950	0.0000200	-0.3180080
C	-2.4431460	-1.1333300	-0.0678360
C	-3.7901990	-0.7698770	-0.6695350
C	-3.7902610	0.7700270	-0.6692670
H	-2.5102060	1.2902840	1.0162520
H	-1.9573570	2.0005740	-0.5132910
H	-1.9574050	-2.0005310	-0.5132670
H	-2.5104320	-1.2901680	1.0161830
H	-3.8776660	-1.1547480	-1.6845080
H	-4.6097380	-1.1894110	-0.0887550
H	-3.8780750	1.1552570	-1.6840720
H	-4.6096730	1.1892710	-0.0880960

21. benzene

C	2.2856110	0.7082530	-0.3623480
C	2.3747640	0.2277580	0.9627420
C	2.0428550	-1.1544870	0.8982690
C	1.7516710	-1.4227120	-0.4447010
N	1.8805110	-0.2847810	-1.2130400
H	2.6753290	0.7921320	1.8309030
H	2.0174110	-1.8615200	1.7126710
C	1.4717450	-2.7415480	-1.0641800
H	0.7063550	-2.6785080	-1.8380490

H	2.3758090	-3.1222150	-1.5436970
H	1.1602230	-3.4719560	-0.3170650
C	2.6446170	2.0558820	-0.8679060
H	3.6859220	2.0651790	-1.1958330
H	2.0243090	2.3247340	-1.7220430
H	2.5280400	2.8144110	-0.0942950
Mn	0.3788040	0.0767800	0.2788810
C	-0.3161020	0.0517330	1.9298040
C	-0.2518240	1.7428330	0.0463720
O	-0.6886060	0.0388340	3.0151080
O	-0.5883290	2.8319800	-0.0788930
C	-1.4793300	-1.3729120	-0.2494290
C	-2.6441380	-1.1747620	0.5230140
C	-3.5443470	-0.2046890	0.1837220
C	-3.3332900	0.5885850	-0.9565530
C	-2.2180510	0.4038770	-1.7235290
C	-1.2612410	-0.5708180	-1.3717930
H	-0.8867070	-2.2605600	-0.0788170
H	-2.8201870	-1.8053230	1.3855360
H	-4.4342870	-0.0588620	0.7824320
H	-4.0622260	1.3403780	-1.2305940
H	-2.0573970	1.0033300	-2.6105980
H	-0.4684330	-0.7957050	-2.0719060

22. bromohexane

C	3.5507480	0.3053240	-1.0298230
C	2.4179600	0.2059400	-1.8610070
C	1.5637390	1.2792560	-1.4813710
C	2.2209050	1.9599270	-0.4441330
N	3.4228310	1.3535790	-0.1528800
H	2.2517740	-0.5252750	-2.6361870
H	0.6027520	1.5311620	-1.9038650
C	1.8046240	3.2069600	0.2435200
H	2.1733700	3.2221420	1.2682580
H	2.2152560	4.0789910	-0.2695610
H	0.7182640	3.3052480	0.2595580
C	4.7913770	-0.5067480	-1.0716840
H	5.2349030	-0.5787440	-0.0795360
H	4.5962410	-1.5116600	-1.4456970
H	5.5245900	-0.0367550	-1.7301540
Mn	1.8543450	-0.0304170	0.1958670
C	2.6531090	-1.4511650	0.9637590
C	1.2501300	0.5382130	1.7897750
O	3.2246370	-2.3215190	1.4442660
O	0.8977400	0.9517880	2.8018790
C	-1.6839410	-0.0985720	0.2361820
H	-1.6165820	-0.0690430	1.3223960
H	-1.4205130	0.8810330	-0.1622230
C	-3.0124400	-0.6006170	-0.2556660
H	-3.1841900	-1.6157210	0.1151330
H	-3.0031630	-0.6670630	-1.3478500
C	-4.1429850	0.3088980	0.1959200
H	-4.1447030	0.3760430	1.2898780
H	-3.9620720	1.3272880	-0.1673560
C	-5.5005480	-0.1646870	-0.2840010
H	-5.4971330	-0.2337800	-1.3785190
H	-5.6800030	-1.1841330	0.0780820
C	-6.6366400	0.7354470	0.1606410
H	-6.6349580	0.8024380	1.2536620
H	-6.4516850	1.7525740	-0.2007780
C	-7.9864240	0.2510420	-0.3259030
H	-8.7963180	0.9041980	-0.0010170
H	-8.0155320	0.2043560	-1.4167140
H	-8.1998270	-0.7526440	0.0481190
Br	-0.2213030	-1.2795070	-0.3345300

(F) $TpRe(CO)_2L$

23. THF

Re	-0.1697620	-0.7053680	0.0362780
C	-0.6165030	-1.9544190	-1.3100470
C	-0.3184120	-2.0871090	1.3210010
O	-0.3926800	-2.9331860	2.1130090
O	-0.8803800	-2.7186400	-2.1449180
N	1.9208590	-0.9401230	-0.2251910
C	2.7076340	-1.9995160	-0.3764570
C	3.9907200	-0.2280260	-0.4653410
C	4.0328810	-1.6000460	-0.5330200
H	2.2766860	-2.9877330	-0.3641270
H	4.7727180	0.5100560	-0.5335460
H	4.8961360	-2.2256030	-0.6744420
N	0.0743940	0.9837220	-1.3852770
C	-0.6267020	1.3943600	-2.4368960
C	-0.0407430	2.5277000	-2.9964210
H	-1.5035440	0.8436040	-2.7436810
C	1.0670720	2.7625720	-2.2110390
H	-0.3676580	3.0859580	-3.8556780
H	1.8277830	3.5238050	-2.2688590
N	0.4408560	0.8279690	1.5308680
C	0.0703390	1.0844230	2.7809380
C	0.8242460	2.1313600	3.3056930
H	-0.7070680	0.4930570	3.2405060
C	1.6819060	2.4793640	2.2851380
H	0.7615670	2.5637490	4.2884940
H	2.4548730	3.2286550	2.2336200
B	2.1532610	1.5845840	-0.1320670
H	3.0351970	2.3909100	-0.2007790
N	1.4343640	1.6882410	1.2316800
N	2.7155380	0.1556620	-0.2806940
N	1.1153010	1.8271960	-1.2519160
O	-2.2618150	0.0439880	0.2719010
C	-3.4025230	-0.7249220	-0.1324760
C	-2.6293340	1.4050410	0.5306340
C	-4.5906190	0.1715170	0.1316080
H	-3.2945500	-0.9656450	-1.1952600
H	-3.3974540	-1.6575460	0.4327500
C	-3.9944210	1.5532380	-0.0971440
H	-1.8637920	2.0557170	0.1064410
H	-2.6608870	1.5621950	1.6138670
H	-4.9262110	0.0711690	1.1660360
H	-5.4315600	-0.0540590	-0.5214040
H	-4.5741850	2.3589270	0.3494550
H	-3.8956310	1.7533040	-1.1671560

(G) CpRu(CO)(Cl)L

24. cyclopentene

C	1.2916530	-1.3074280	1.5085750
C	0.4288710	-2.0480010	0.6648660
C	0.9725640	-1.9887530	-0.6621410
C	2.3445850	-0.7609440	0.7118940
C	2.1382260	-1.2083480	-0.6214660
H	1.1711910	-1.1748950	2.5719850
H	-0.4319680	-2.6164180	0.9765150
H	0.5530790	-2.4491210	-1.5420050
H	3.1609630	-0.1473850	1.0538800
H	2.7240390	-0.9057600	-1.4747270
Ru	0.4220740	0.0743040	0.0603680
C	0.0768030	1.3900140	1.3509210
O	-0.1127600	2.1513150	2.1823230
Cl	1.0988760	1.7698600	-1.5182030
C	-2.9051020	-0.9736910	0.3756290
C	-2.3299990	-1.2731360	-1.0108890
C	-1.4011840	-0.1175890	-1.2841290
C	-1.6950050	0.9221800	-0.4201290
C	-2.8281210	0.5480610	0.4913700
H	-2.2831700	-1.4281100	1.1483860
H	-3.1241640	-1.2367450	-1.7663410
H	-1.8771360	-2.2621840	-1.0925660
H	-0.9566010	0.0463080	-2.2572820

H	-1.4713530	1.9530350	-0.6608870
H	-3.7371120	1.0112370	0.0893300
H	-2.7219190	0.9069520	1.5156750
H	-3.9156570	-1.3586350	0.5057160

25. cylcohexene

C	-2.4973340	0.5395050	-1.0779230
C	-2.0062980	-0.7018580	-1.5484140
C	-2.0392620	-1.6352060	-0.4623870
C	-2.8000980	0.3908050	0.3138190
C	-2.5247810	-0.9533250	0.6698110
H	-2.6284720	1.4333130	-1.6660660
H	-1.6915990	-0.9159170	-2.5587020
H	-1.7379010	-2.6690330	-0.4977380
H	-3.1959030	1.1486650	0.9693840
H	-2.5872770	-1.3573060	1.6677350
Ru	-0.6454970	0.0778170	-0.0097400
C	-0.0855170	1.8510980	0.1896590
O	0.1844320	2.9539310	0.3155890
Cl	0.2778050	-0.2774220	2.1922190
C	2.1833420	-1.7470520	0.0155620
C	1.1171820	-1.1874620	-0.8817030
C	1.1899990	0.0685180	-1.4552380
C	2.3707960	0.9628450	-1.2065750
C	3.1263530	0.5918290	0.0561940
C	3.4459010	-0.8927730	0.0442580
H	0.4909530	-1.9229730	-1.3747500
H	1.7917220	-1.8663260	1.0277910
H	2.4219620	-2.7535070	-0.3401280
H	3.0382200	0.8388790	-2.0703380
H	2.0860500	2.0161320	-1.2099690
H	4.0440790	1.1793740	0.1201930
H	2.5286430	0.8315170	0.9409660
H	4.0536550	-1.1087810	-0.8424960
H	4.0519290	-1.1646890	0.9100000
H	0.6559650	0.2498720	-2.3821390

26. cyclooctene

C	-3.1036010	0.1204180	-0.9315180
C	-2.3298510	-0.8712720	-1.5840960
C	-2.0185180	-1.8791180	-0.6090190
C	-3.2360850	-0.2395730	0.4451400
C	-2.5704880	-1.4853060	0.6194650
H	-3.5146090	1.0031330	-1.3950800
H	-2.0806450	-0.8987350	-2.6328070
H	-1.4430390	-2.7741070	-0.7821950
H	-3.7681230	0.3048830	1.2071210
H	-2.4339750	-1.9898210	1.5627320
Ru	-1.1266600	0.1063060	-0.0290510
C	-1.0043410	1.9790660	-0.0258420
O	-0.9998730	3.1214690	-0.0405600
Cl	-0.1307730	0.1332320	2.1802230
C	4.3691410	0.4324520	-0.0857650
C	3.8745440	-0.8270950	0.6135320
C	0.9617640	0.5591060	-1.0041380
C	3.0712490	-1.8231050	-0.2285810
C	0.8045250	-0.8107520	-0.9015260
C	1.5502860	-1.7626690	-0.0086450
H	5.2116380	0.1767050	-0.7366240
H	3.2772480	-0.5516360	1.4880930
H	3.3114780	-1.7151280	-1.2923480
H	0.6608520	0.9963510	-1.9522720
H	0.3832760	-1.2793410	-1.7874040
H	4.7773430	1.0979740	0.6811240
H	4.7539990	-1.3327640	1.0201670
H	3.3885380	-2.8333870	0.0390510
H	1.1303510	-2.7571070	-0.1819180
H	1.3581660	-1.5341530	1.0407450
C	3.3488190	1.2005240	-0.9168950
H	3.2179690	0.6990120	-1.8815020
H	3.7697270	2.1783350	-1.1603770
C	1.9699740	1.3725790	-0.2529130
H	1.9948980	1.0814190	0.7976280
H	1.6755650	2.4226910	-0.2703910

27. THF

C	-2.6700830	0.0817540	-0.7765660
C	-1.9026850	-0.7960710	-1.5904010
C	-1.4696130	-1.8716260	-0.7489820
C	-2.6604100	-0.4104460	0.5639020
C	-1.9330670	-1.6480060	0.5506470
H	-3.1617240	0.9820280	-1.1102340
H	-1.7379190	-0.7095700	-2.6513760
H	-0.8348210	-2.6884190	-1.0572880
H	-3.1632130	0.0209030	1.4132850
H	-1.7022760	-2.2437660	1.4193180
Ru	-0.6712020	0.1092510	-0.0176310
C	-0.5710060	1.9652380	-0.2276660
O	-0.6310970	3.0982250	-0.3856570
Cl	0.4044760	0.1721100	2.1393560
C	2.0854030	-1.4100110	-0.2771050
O	1.4337230	-0.1941050	-0.6976710
C	2.3617740	0.8998200	-0.6231700
C	3.7180590	0.2479250	-0.7074800
C	3.4904260	-1.0094820	0.1190130
H	1.5200830	-1.8377230	0.5516500
H	2.0701210	-2.0954650	-1.1299510
H	2.1259000	1.5818160	-1.4405620
H	2.2245300	1.4130270	0.3341040
H	3.9606970	-0.0050910	-1.7421560
H	4.5088860	0.8843610	-0.3143020
H	4.2170120	-1.7967010	-0.0749780
H	3.5157080	-0.7658410	1.1826330

(H) (μ-pdt)$Fe_2(CO)_5$L

28. 3-hexyne

Fe	-0.6607710	-0.4656660	0.5780870
Fe	1.3593710	0.7764400	-0.3350310
C	-1.2224840	-2.0963590	1.0059580
O	-1.5137460	-3.1698300	1.2650860
C	-1.2094710	0.3088170	2.1102490
O	-1.5238930	0.7354960	3.1181250
C	0.8392950	1.7411670	-1.7539050
O	0.5153080	2.3267740	-2.6755320
C	1.1532810	2.1410730	0.8112420
O	1.0156440	3.0099550	1.5370430
C	3.1175890	0.8410560	-0.7039920
O	4.2364890	0.9170100	-0.9055440
S	1.3976580	-0.5875500	1.4833940
S	0.3582680	-0.9864440	-1.3851640
C	2.1913830	-2.1940890	1.1149310
H	1.5263010	-2.9610090	1.5202640
H	3.0977090	-2.1977470	1.7220330
C	2.5270140	-2.4769550	-0.3270430
H	3.2382560	-1.7346970	-0.6960810
H	3.0425900	-3.4425890	-0.3743070
C	1.3303850	-2.5290970	-1.2419280
H	1.6438900	-2.7672960	-2.2588930
H	0.6297340	-3.3069970	-0.9259340
C	-2.4553910	-0.3077200	-0.6333370
C	-2.1176420	0.8606010	-0.4455840
H	-3.8073970	-0.4503100	-3.0013260
H	-3.4826190	2.4670560	1.3054770
C	-3.2139030	-1.4379770	-1.1730690
H	-2.5230000	-2.1378480	-1.6529500
H	-3.6780040	-1.9919110	-0.3515060
C	-4.2696900	-0.9711560	-2.1626570
H	-4.9717140	-0.2847190	-1.6883810

H	-4.8344390	-1.8164950	-2.5553420
C	-2.6082820	2.9528520	0.8711610
H	-1.7930170	2.8865610	1.5896320
H	-2.8391240	4.0086260	0.7324970
C	-2.2330190	2.3248060	-0.4611690
H	-1.3145810	2.7804460	-0.8319850
H	-3.0058000	2.5553500	-1.2029030

29. cyclohexene

Fe	0.5744200	0.6534790	0.1478820
Fe	-1.3872610	-0.9506110	-0.0047870
C	0.9966710	2.3810910	0.1866900
O	1.2109580	3.5023590	0.2136830
C	1.4110330	0.1280820	1.6541630
O	1.8551840	-0.1950090	2.6527880
C	-0.9125030	-2.2068210	-1.1897440
O	-0.6017860	-2.9977250	-1.9486150
C	-0.8597450	-1.9863580	1.3635520
O	-0.5098010	-2.6445390	2.2251090
C	-3.1598600	-1.2638270	-0.0505980
O	-4.2753600	-1.4945800	-0.0510220
S	-1.2711110	0.8022180	1.4367410
S	-0.8686080	0.6190490	-1.5963550
C	-2.3298040	2.2029270	0.9250050
H	-1.7074690	3.0985550	0.9975900
H	-3.0877750	2.2710300	1.7065840
C	-2.9808450	2.1059710	-0.4304360
H	-3.6415060	1.2370130	-0.4654010
H	-3.6238120	2.9828050	-0.5651440
C	-2.0042790	2.0503560	-1.5772020
H	-2.5385190	2.0092490	-2.5269420
H	-1.3728290	2.9426420	-1.5946690
C	2.3772620	0.6276050	-1.2113590
C	1.8688710	-0.6463580	-1.1535690
H	2.0035190	1.2834090	-1.9896300
H	1.1462760	-0.9183040	-1.9107450
C	3.7213610	0.9894190	-0.6489420
H	4.3642280	1.1846210	-1.5169280
H	3.6898000	1.9325920	-0.0982990
C	4.3567830	-0.1115640	0.1885620
H	3.9570870	-0.1046020	1.2049460
H	5.4261410	0.0851840	0.2858550
C	4.1200190	-1.4729440	-0.4400900
H	4.6368850	-2.2531110	0.1213170
H	4.5447650	-1.4779780	-1.4505300
C	2.6319950	-1.7865490	-0.5230360
H	2.2503310	-2.0367750	0.4698290
H	2.4669500	-2.6814200	-1.1280000

30. 2,3-dihydrofuran

Fe	0.8315000	0.2085080	0.5950710
Fe	-1.4519030	-0.6013870	-0.1416210
C	1.8420010	1.6652420	0.7730820
O	2.4104400	2.6503970	0.8720000
C	0.9251370	-0.4829600	2.2611560
O	0.9711380	-0.9123410	3.3155030
C	-1.0516200	-2.1027080	-1.0289000
O	-0.7835060	-3.0624100	-1.5831200
C	-1.8925900	-1.5382400	1.3265780
O	-2.1681150	-2.1240280	2.2634770
C	-3.0841100	-0.2993620	-0.8425870
O	-4.1267830	-0.1444740	-1.2746070
S	-1.1032920	1.1542760	1.2641230
S	0.0295220	0.4952350	-1.4975680
C	-1.3762690	2.7751610	0.4651270
H	-0.5093010	3.3909950	0.7177570
H	-2.2369290	3.1968070	0.9860730
C	-1.6150300	2.7619150	-1.0218900
H	-2.5151140	2.1866370	-1.2492000
H	-1.8181670	3.7878650	-1.3483730
C	-0.4523540	2.2298330	-1.8193280
H	-0.6748830	2.2722760	-2.8860710
H	0.4444660	2.8311170	-1.6467810
O	3.8135190	-0.1650830	-0.5729200
C	3.0002930	-0.7169360	0.3325800
C	3.2878910	-0.4917220	-1.8743850
C	2.0183020	-1.5247420	-0.1818200
H	3.3553210	-0.6482210	1.3505080
C	2.3282100	-1.6531730	-1.6548120
H	2.7632350	0.3897200	-2.2518960
H	4.1328030	-0.7119480	-2.5238190
H	1.5832690	-2.3382730	0.3775480
H	1.4665930	-1.5846770	-2.3172060
H	2.8068180	-2.6199530	-1.8345500

Monomer Complex without Ligand

(A) $CpMn(CO)_2$

C	-1.6363700	1.1506690	-0.0683240
C	-1.9739300	-0.0000360	-0.8116880
C	-1.6363440	-1.1507120	-0.0682920
C	-1.0686720	0.7051720	1.1631020
C	-1.0686540	-0.7051700	1.1631210
H	-1.7887550	2.1740820	-0.3685560
H	-2.3761040	-0.0000560	-1.8144020
H	-1.7887020	-2.1741400	-0.3684880
H	-0.7002340	1.3360990	1.9558960
H	-0.7002000	-1.3360610	1.9559360
C	1.3250570	1.3204320	-0.1274990
O	2.0355810	2.1802770	0.1352830
C	1.3250980	-1.3204050	-0.1274880
O	2.0356700	-2.1802140	0.1352790
Mn	0.1274750	-0.0000050	-0.4104990

(B) $BzCr(CO)_2$

C	1.4379190	1.3282810	-0.1991620
O	2.2025060	2.1640470	-0.0119700
C	1.4381790	-1.3281340	-0.1991210
O	2.2030680	-2.1636450	-0.0120270
C	-1.3593820	1.4091830	0.2946160
C	-0.7945400	0.7029360	1.3846950
C	-0.7944190	-0.7025410	1.3849870
C	-1.3590960	-1.4093110	0.2951760
C	-1.8553240	-0.7109380	-0.8088960
C	-1.8554610	0.7102670	-0.8091720
H	-1.3211400	2.4895710	0.2736740
H	-0.3395330	1.2429110	2.2026920
H	-0.3393210	-1.2421000	2.2032060
H	-1.3206380	-2.4897010	0.2746570
H	-2.2070420	-1.2537390	-1.6756620
H	-2.2072630	1.2526530	-1.6761640
Cr	0.1392950	-0.0000530	-0.3945490

(C) $Cr(CO)_5$

Cr	-0.0001810	0.0008410	-0.3825940
C	0.3465760	-1.8858620	-0.3876310
C	-0.3471300	1.8878430	-0.3888290
C	-1.8867840	-0.3481050	-0.3898780
C	-0.0003600	0.0014550	1.4620240
C	1.8872140	0.3455020	-0.3897250
O	0.5523670	-3.0036340	-0.3440650
O	-0.5521180	3.0057650	-0.3460240
O	-3.0042340	-0.5557950	-0.3487330
O	-0.0006050	0.0018630	2.6056540
O	3.0054960	0.5486530	-0.3485190

(D) $CpRe(CO)_2$

C	1.8528080	-1.1563800	0.0928700
C	2.1955050	-0.0000420	-0.6458300

C	1.8528330	1.1563310	0.0928290
C	1.2278750	-0.7148340	1.3016780
C	1.2278930	0.7148410	1.3016530
H	2.0311680	-2.1775470	-0.1994110
H	2.6372990	-0.0000630	-1.6311910
H	2.0312140	2.1774840	-0.1994890
H	0.8743250	-1.3431990	2.1028210
H	0.8743540	1.3432440	2.1027710
C	-1.4062030	-1.3687540	0.0586250
O	-2.1120140	-2.2234010	0.3730570
C	-1.4061300	1.3688050	0.0586150
O	-2.1118740	2.2235100	0.3730460
Re	-0.1056630	-0.0000080	-0.2894260

(E) (DMP)Mn(CO)$_2$

C	1.1001500	-1.2201080	-0.2546800
C	0.7115730	-1.5313510	1.0620640
C	-0.7141420	-1.5298760	1.0624200
C	-1.1027770	-1.2178810	-0.2540910
N	-0.0012840	-0.9986080	-1.0490020
H	1.3724050	-1.7476420	1.8871210
H	-1.3750120	-1.7446800	1.8878400
C	-2.4715230	-1.1814020	-0.8228380
H	-2.5315360	-0.4541450	-1.6314000
H	-2.7289320	-2.1581020	-1.2373040
H	-3.2121480	-0.9305480	-0.0637940
C	2.4687300	-1.1859810	-0.8240040
H	2.5293180	-0.4593710	-1.6331110
H	3.2099910	-0.9355180	-0.0654530
H	2.7247460	-2.1633170	-1.2378410
Mn	0.0006740	0.4047390	0.5355660
C	1.3149560	1.5622520	0.0707420
C	-1.3118260	1.5640510	0.0703170
O	2.1622590	2.2428290	-0.2877850
O	-2.1582030	2.2455310	-0.2886860

(F) TpRe(CO)$_2$

Re	-0.8408700	-0.0000430	-0.5297640
C	-2.1884610	-1.3282800	-0.3500570
C	-2.1886330	1.3280350	-0.3500880
O	-3.0044900	2.1375540	-0.2176560
O	-3.0048520	-2.1372490	-0.2175630
N	-0.3673550	-0.0000040	1.4920140
C	-1.1054470	-0.0000130	2.5978660
C	0.9966000	0.0000410	3.2128380
C	-0.2821580	0.0000210	3.7190650
H	-2.1807920	-0.0000380	2.5227070
H	1.9542760	0.0000660	3.7064490
H	-0.5809280	0.0000250	4.7520110
N	0.8081180	-1.4618150	-0.7202480
C	0.9428610	-2.6198740	-1.3604110
C	2.1958350	-3.1694930	-1.1075310
H	0.1302480	-3.0019750	-1.9584790
C	2.8023140	-2.2658550	-0.2626420
H	2.5983080	-4.0945830	-1.4799650
H	3.7742060	-2.2740400	0.2031280
N	0.8080580	1.4617990	-0.7202760
C	0.9427490	2.6198500	-1.3604620
C	2.1956720	3.1695670	-1.1075350
H	0.1301320	3.0018850	-1.9585660
C	2.8021930	2.2659730	-0.2626300
H	2.5980890	4.0946840	-1.4799620
H	3.7740730	2.2742290	0.2031660
B	2.0933030	0.0000380	0.8472800
H	3.1455080	0.0000650	1.4158920
N	1.9556110	1.2509200	-0.0443270
N	0.9326530	0.0000250	1.8715470
N	1.9556630	-1.2508660	-0.0443080

(G) CpRu(CO)(Cl)

C	-1.6208660	1.2548240	0.0007000
C	-1.6243360	0.4180040	-1.1448470
C	-1.7543900	-0.9442670	-0.6973440
C	-1.6231220	0.4174230	1.1457940
C	-1.7536750	-0.9446280	0.6977730
H	-1.5552090	2.3307170	0.0009500
H	-1.5979300	0.7447600	-2.1715610
H	-1.7618960	-1.8143570	-1.3341260
H	-1.5953830	0.7436030	2.1726580
H	-1.7603770	-1.8150220	1.3341480
Ru	0.1374510	-0.0221060	-0.0004150
C	1.3386390	1.4519020	-0.0002290
O	1.9235530	2.4311060	0.0003300
Cl	1.7094720	-1.6814950	0.0001440

(H) (μ-pdt)Fe$_2$(CO)$_5$

Fe	1.1784560	0.6505560	0.4587540
Fe	-1.1964170	0.0626840	0.0274080
C	2.9145950	0.2189480	0.4555790
O	3.9981910	-0.1243200	0.3629020
C	1.2862460	2.3346510	-0.1983210
O	1.3288860	3.3911940	-0.6182200
C	-1.9449690	0.7155600	1.5271720
O	-2.4066530	1.1298790	2.4810960
C	-1.7311150	1.4974950	-0.9076850
O	-2.0519900	2.4113070	-1.5050720
C	-2.4673990	-1.1314630	-0.4584980
O	-3.2876950	-1.8627490	-0.7544450
S	0.4903120	-0.1132570	-1.4851680
S	0.2148220	-1.0802690	1.4284140
C	1.0749590	-1.8363120	-1.6694550
H	2.1646170	-1.7936220	-1.5913960
H	0.8363680	-2.0963120	-2.7022320
C	0.5010550	-2.8645470	-0.7277680
H	-0.5839220	-2.9099220	-0.8450210
H	0.8803770	-3.8485760	-1.0247790
C	0.8472500	-2.6474050	0.7260510
H	0.4288400	-3.4448180	1.3401750
H	1.9289110	-2.6386060	0.8785760