## Insight into metal-phosphorus bonding from analysis of the electronic structure of redox pairs of metal-phosphine complexes

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## Supporting Information

Tables containing relative energies of different spin states of the target compounds (S1 and S2), followed by Tables containing the average bond lengths and angles in reduced and oxidized complexes, together with the changes in bond lengths and angles (S3 to S15)

	Table S1	B3LYP Con	mputed relative	energies (	(kcal mol <sup>-1</sup> )	) for different s	pin states	of the target	compounds.
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Compound	charge	Oxidation	on multiplicity					
		state	1	2	3	4	5	6
<i>trans</i> –[MoCl <sub>2</sub> (dmpe) <sub>2</sub> ]	+1	III $(d^3)$		5.43		0.00		/
	0	II $(d^4)$	12.74		0.00		48.42	
$trans-[CrCl_2(dmpe)_2]$	+1	$III (d^3)$		31.92		0.00		
	0	II $(d^4)$	27.34		0.00		-0.54	
<i>trans</i> –[TcCl <sub>2</sub> (dppe) <sub>2</sub> ]	+1	$III (d^4)$	19.15		0.00		36.42	
	0	II $(d^{\circ})$		0.00		34.09		49.72
$[Mn(CO)(dppe)(\eta^{5}-C_{6}H_{6}Ph)]$	+1	$II (d^5)$		0.00		11.69		14.48
	0	$I(d^6)$	0.00		22.42		39.21	
$[FeCp^*(C \equiv C - C_6H_4NO_2)(dppe)]$	+1	III $(d^5)$		0.00		16.57		41.00
	0	II $(d^6)$	0.00		11.44		15.66	
$[Fe(P(CH_2CH_2PPh_2)_3)(C\equiv C-Ph)]$	+1	II $(d^6)$	14.03		0.00		10.30	
	0	$I(d^7)$		0.00		9.11		
[FeCp*(dppe)]	+1	II $(d^6)$	14.16		0.00		-0.26	
	0	$I(d^7)$		0.00		4.20		
[Cp*MoCl <sub>2</sub> (PMe <sub>2</sub> Ph) <sub>2</sub> ]	+1	$IV (d^2)$	12.47	0.00				
	0	III $(d^3)$		0.00		17.86		
$[\eta^7 - (C_7 H_7) Mo(C \equiv CPh)(dppe)]$	+1	$I(d^5)$		0.00		29.95		52.46
	0	$0 (d^6)$	0.00		33.15		50.32	

## **Table S2** BP86 relative single-point energies (kcal mol<sup>-1</sup>) for different spin states of target compounds.

Compound	charge Oxidation		multiplicity					
		state	1	2	3	4	5	6
<i>trans</i> –[CrCl <sub>2</sub> (dmpe) <sub>2</sub> ]	+1	III $(d^3)$		22.27		0.00		
	0	$II (d^4)$	24.74		0.00		16.37	
$[Mn(CO)(dppe)(\eta^5-C_6H_6Ph)]$	+1	II $(d^5)$		0.00		24.57		50.16
	0	$I(d^6)$	0.00		34.78		67.94	
$[FeCp^{*}(C=C-C_{6}H_{4}NO_{2})(dppe)]$	+1	III $(d^5)$		0.00		28.63		66.37
	0	II $(d^6)$	0.00		28.08		50.43	
$[Fe(P(CH_2CH_2PPh_2)_3)(C=C-Ph)]$	+1	II $(d^6)$	4.38		0.00		30.65	
	0	$I(d^7)$		0.00		29.36		
[FeCp*(dppe)]	+1	II $(d^6)$	5.00		0.00		0.36	
	0	$I(d^{7})$		0.00		20.62		

## # Supplementary Material (ESI) for New Journal of Chemistry # This journal is © The Royal Society of Chemistry and # The Centre National de la Recherche Scientifique, 2005

In Tables S3 – S15, all bond lengths are averages of the relevant values throughout the structure. E.g. for *trans*- $[MoCl_2(dmpe)_2]$ , r(Mo-Cl) refers to the average of the two Mo-Cl distances, r(Mo-P) is the average of the four Mo-P distances, r(P-Me) is the average of the eight P-C(Me) distances,  $r(P-CH_2)$  is the average of the four P-C(CH\_2) distances, and  $\alpha(MePMe)$  is the average of the 4 C(Me)-P-C(Me) angles. Also, distances to rings refer to distances between a metal and the centroid of a ligand.

**Table S3.** Experimental and computational average bond lengths (Å) and angles (degrees) for reduced and oxidized *trans*-[MoCl<sub>2</sub>(dmpe)<sub>2</sub>], and changes upon oxidation. In this case, as discussed in ref. 15 of the paper, some of the crystal structures seem to be affected by disorder, and the agreement between experiment and theory is poor. However, the computed trends are in good agreement with those found for the other complexes, and are probably more reliable than the experimental values.

		Calculated		Experimental			
	Reduced	Oxidized	Change	Reduced	Oxidized	Change	
r(Mo–Cl) r(Mo–P)	2.498 2.515	2.443 2.605	-0.055 0.090	2.443 2.463	2.436 2.462	-0.007 -0.001	
r(P–Me)	1.852	1.842	-0.010	1.806	1.818	0.013	
r(P–CH <sub>2</sub> )	1.880	1.865	-0.015	1.819	1.841	0.022	
a(MePMe)	102.5	104.70	2.20	101.75	101.30	-0.45	

**Table S4.** Experimental and computational average bond lengths (Å) and angles (degrees) for reduced and oxidized *trans*-[CrCl<sub>2</sub>(dmpe)<sub>2</sub>], and changes upon oxidation.

		Calculated		Experimental			
	Reduced	Oxidized	Change	Reduced	Oxidized	Change	
r(Cr–Cl)	2.402	2.328	-0.074	2.345	2.292	-0.053	
r(Cr–P)	2.444	2.515	0.071	2.370	2.445	0.076	
r(P–Me)	1.851	1.840	-0.010	1.824	1.809	-0.015	
r(P–CH <sub>2</sub> )	1.875	1.862	-0.013	1.858	1.821	-0.037	
a(MePMe)	102.30	104.80	2.50	100.85	103.70	2.85	

**Table S5.** Experimental and computational average bond lengths (Å) and angles (degrees) for reduced and oxidized *trans*- $[TcCl_2(dppe)_2]$ , and changes upon oxidation.

		Calculated		Experimental			
	Reduced	Oxidized	Change	Reduced	Oxidized	Change	
r(Tc–Cl)	2.493	2.372	-0.121	2.424	2.319	-0.105	
r(Tc–P)	2.475	2.541	0.066	2.429	2.501	0.072	
r(P–Ph)	1.853	1.840	-0.013	1.838	1.827	-0.011	
r(P–CH <sub>2</sub> )	1.880	1.876	-0.004	1.850	1.839	-0.011	
a(PhPPh)	102.10	104.95	2.85	100.80	101.65	0.85	

		Calculated			Experimental			
	Reduced	Oxidized	Change	Reduced	Oxidized	Change		
$r(Mn-(\eta^5-C_6H_6Ph))$	1.676	1.675	-0.001	1.703	1.708	0.005		
r(Mn–P)	2.273	2.394	0.121	2.221	2.334	0.112		
r(Mn–C(CO))	1.770	1.811	0.041	1.773	1.803	0.030		
r(C–O)	1.172	1.155	-0.017	1.176	1.145	-0.031		
r(P–Ph)	1.856	1.836	-0.020	1.850	1.817	-0.033		
r(P–CH <sub>2</sub> )	1.882	1.867	-0.015	1.864	1.827	-0.037		
a(PhPPh)	100.81	104.74	3.93	98.66	104.14	5.49		

**Table S6.** Experimental and computational average bond lengths (Å) and angles (degrees) for reduced and oxidized  $[Mn(CO)(dppe)(\eta^5-C_6H_6Ph)]$ , and changes upon oxidation.

**Table S7.** Experimental and computational average bond lengths (Å) and angles (degrees) for reduced and oxidized  $[FeCp^*(C=C-C_6H_4NO_2)(dppe)]$ , and changes upon oxidation.

		Calculated		Experimental			
	Reduced	Oxidized	Change	Reduced	Oxidized	Change	
r(Fe–Cp*)	1.792	1.808	0.016	1.739	1.780	0.041	
r(Fe–C(CC))	1.890	1.892	0.002	1.876	1.893	0.017	
r(Fe–P)	2.260	2.350	0.090	2.188	2.271	0.083	
r(C–C)	1.237	1.231	-0.006	1.220	1.214	-0.005	
r(P–Ph)	1.856	1.842	-0.014	1.840	1.823	-0.017	
r(P–CH <sub>2</sub> )	1.879	1.869	-0.010	1.848	1.843	-0.005	
a(PhPPh)	100.83	102.82	1.98	99.77	102.25	2.47	

**Table S8.** Experimental and computational average bond lengths (Å) and angles (degrees) for reduced and oxidized  $[Fe(P(CH_2CH_2PPh_2)_3)(C=C-Ph)]$ , and changes upon oxidation. The phosphorus atom that is not linked to any of the phenyl groups is represented by P\*.

		Calculated			Experimental			
	Reduced	Oxidized	Change	Reduced	Oxidized	Change		
r(Fe–C)	1.925	1.907	-0.018	1.916	1.882	-0.034		
r(Fe–P)	2.277	2.414	0.136	2.204	2.302	0.098		
r(Fe–P*)	2.186	2.290	0.105	2.153	2.224	0.071		
r(C–C)	1.237	1.233	-0.004	1.213	1.202	-0.011		
r(P–Ph)	1.853	1.838	-0.014	1.840	1.817	-0.023		
$r(P-CH_2)$	1.890	1.867	-0.023	1.842	1.847	0.005		
r(P*CH <sub>2</sub> )	1.874	1.863	-0.012	1.833	1.805	-0.028		
α(PhPPh)	100.06	104.36	4.29	99.22	103.00	3.79		
$\alpha(CH_2P*CH_2)$	105.59	105.86	0.28	105.71	105.38	-0.33		

			Calculated		Experimental			
		Reduced	Oxidized	Change	Reduced	Oxidized	Change	
-	r(Fe–Cp*)	1.808	1.820	0.012	1.722	1.768	0.046	
	r(Fe–P)	2.186	2.317	0.130	2.137	2.246	0.110	
	r(P–Ph)	1.859	1.833	-0.026	1.844	1.806	-0.038	
	$r(P-CH_2)$	1.887	1.875	-0.012	1.855	1.830	-0.025	
	a(PhPPh)	101.65	106.04	4.39	100.40	104.45	4.05	

**Table S9.** Experimental and computational average bond lengths (Å) and angles (degrees) for reduced and oxidized [FeCp\*(dppe)], and changes upon oxidation.

**Table S10.** Experimental and computational average bond lengths (Å) and angles (degrees) for reduced and oxidized  $[Cp^*MoCl_2(PMe_2Ph)_2]$ , and changes upon oxidation.  $\alpha(MePPh)$  is the average of the 4 C(Me)–P–C(Ph) angles.

		Calculated		Experimental			
	Reduced	Oxidized	Change	Reduced	Oxidized	Change	
r(Mo–Cl)	2.551	2.433	-0.118	2.480	2.383	-0.097	
r(Mo–Cp*)	2.023	2.087	0.064	1.966	2.034	0.068	
r(Mo–P)	2.573	2.625	0.051	2.527	2.566	0.039	
r(P–Me)	1.851	1.843	-0.008	1.817	1.804	-0.014	
r(P–Ph)	1.844	1.832	-0.012	1.823	1.811	-0.012	
a(MePMe)	101.20	102.54	1.34	101.17	102.39	1.22	
a(MePPh)	102.85	104.81	1.96	102.23	104.62	2.39	

**Table S11.** Experimental and computational average bond lengths (Å) and angles (degrees) for reduced and oxidized  $[\eta^7 - (C_7H_7)Mo(C = CPh)(dppe)]$ , and changes upon oxidation.

		Calculated		Experimental			
	Reduced	Oxidized	Change	Reduced	Oxidized	Change	
$r(Mo-\eta^7)$	1.672	1.682	0.010	1.636	1.624	-0.012	
r(Mo–C(CC))	2.131	2.075	-0.056	2.137	2.067	-0.070	
r(Mo–P)	2.502	2.567	0.065	2.472	2.533	0.061	
r(C–C)	1.235	1.237	0.001	1.205	1.195	-0.011	
r(P–Ph)	1.853	1.841	-0.012	1.838	1.817	0.021	
r(PCH <sub>2</sub> )	1.878	1.873	-0.006	1.845	1.829	-0.016	
α(PhPPh)	101.19	103.09	1.90	100.42	102.00	1.59	

**Table S12.** Computational average bond lengths (Å) and angles (degrees) for reduced and oxidized  $[Cr(CO)_5PH_3]$ , and changes upon oxidation.  $r(Cr-C_{cis})$  refers to the average of the four *cis* Cr–C distances,  $r(C_{cis}-O)$  refers to the average of the four *cis* C–O distances.

Reduced	Oxidized	Change
1.912	1.975	0.063
1.153	1.140	-0.014
1.880	1.983	0.104
1.155	1.137	-0.018
2.400	2.493	0.094
1.416	1.409	-0.007
96.83	99.89	3.06
	Reduced 1.912 1.153 1.880 1.155 2.400 1.416 96.83	ReducedOxidized1.9121.9751.1531.1401.8801.9831.1551.1372.4002.4931.4161.40996.8399.89

**Table S13.** Computational average bond lengths (Å) and angles (degrees) for reduced and oxidized  $[Mo(CO)_5PH_3]$ , and changes upon oxidation.  $r(Mo-C_{cis})$  refers to the average of the four *cis* Mo-C distances,  $r(C_{cis}-O)$  refers to the average of the four *cis* C–O distances.

	Reduced	Oxidized	Change
$r(Mo-C_{cis})$	2.057	2.118	0.043
$r(C_{cis}-O)$	1.153	1.140	-0.012
r(Mo–C <sub>trans</sub> )	2.035	2.117	0.082
$r(C_{trans}-O)$	1.155	1.139	-0.016
r(Mo–P)	2.547	2.604	0.058
r(P–H)	1.416	1.409	-0.006
$\alpha$ (HPH)	96.80	99.88	3.09

**Table S14.** Computational average bond lengths (Å) and angles (degrees) for reduced and oxidized  $[Cr(CO)_5NH_3]$ , and changes upon oxidation.  $r(Cr-C_{cis})$  refers to the average of the four *cis* Cr–C distances,  $r(C_{cis}-O)$  refers to the average of the four *cis* C–O distances.

	Reduced	Oxidized	Change
$r(Cr-C_{cis})$	1.913	1.981	0.068
$r(C_{cis}-O)$	1.155	1.140	-0.015
$r(Cr-C_{trans})$	1.869	1.987	0.118
$r(C_{trans}-O)$	1.158	1.138	-0.020
r(Cr–N)	2.239	2.190	-0.050
r(N–H)	1.019	1.022	0.003
α(HNH)	106.76	105.75	-1.01

**Table S15.** Computational average bond lengths (Å) and angles (degrees) for reduced and oxidized [Mo(CO)<sub>5</sub>NH<sub>3</sub>], and changes upon oxidation.  $r(Mo-C_{cis})$  refers to the average of the four *cis* Mo-C distances,  $r(C_{cis}-O)$  refers to the average of the four *cis* C–O distances.

	Reduced	Oxidized	Change
$r(Mo-C_{cis})$	2.072	2.119	0.046
$r(C_{cis}-O)$	1.154	1.141	-0.014
r(Mo–C <sub>trans</sub> )	2.010	2.100	0.090
$r(C_{trans}-O)$	1.159	1.141	-0.018
r(Mo–P)	2.385	2.328	-0.057
r(P–H)	1.019	1.022	0.004
α(HNH)	106.77	105.78	-0.99

**Table S16.** Computational average bond lengths (Å) and angles (degrees) for reduced and oxidized  $[Cr(CO)_5PMe_3]$ , and changes upon oxidation.  $r(Cr-C_{cis})$  refers to the average of the four *cis* Cr–C distances,  $r(C_{cis}-O)$  refers to the average of the four *cis* Cr–C distances.

	Reduced	Oxidized	Change
$r(Cr-C_{cis})$	1.906	1.963	0.057
$r(C_{cis}-O)$	1.156	1.142	-0.014
$r(Cr-C_{trans})$	1.878	1.980	0.102
r(C <sub>trans</sub> –O)	1.156	1.138	-0.018
r(Cr-P)	2.426	2.500	0.074
r(P–C)	1.850	1.843	-0.008
a(CPC)	101.60	104.00	2.04

**Table S17.** Computational average bond lengths (Å) and angles (degrees) for reduced and oxidized [Mo(CO)<sub>5</sub>PMe<sub>3</sub>], and changes upon oxidation.  $r(Mo-C_{cis})$  refers to the average of the four *cis* Mo-C distances,  $r(C_{cis}-O)$  refers to the average of the four *cis* C–O distances.

	Reduced	Oxidized	Change
r(Mo–C <sub>cis</sub> )	2.071	2.110	0.040
$r(C_{cis}-O)$	1.155	1.143	-0.012
r(Mo–C <sub>trans</sub> )	2.039	2.130	0.091
$r(C_{trans}-O)$	1.156	1.140	-0.016
r(Mo-P)	2.569	2.616	0.047
r(P–C)	1.851	1.843	-0.008
a(CPC)	101.77	103.90	2.13