

The “Silent CO”: a new technique for calculating transition metal carbonyl force fields

Electronic Supplementary Information

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1 Ni(CO)₄ – the model system

Ni(CO)₃(L) data used to calculate $\nu(a_1)$ for Ni(CO)₄.

Table S1: Ni(CO)₃L molecules used to calculate an EFFF for Ni(CO)₄					
Molecule	$\nu(a_1)$	$\nu(e)$	$K(a_1)$	$K(e)$	Ref.
Ni(CO) ₃ (PF ₃)	2111	2049	1800	1696	P. S. Braterman, "Metal Carbonyl Spectra" Table 7.14 (p212) and references therein
Ni(CO) ₃ (PCl ₃)	2103	2044	1786	1688	
Ni(CO) ₃ (POMe ₃)	2082	2010	1751	1632	
Ni(CO) ₃ (POBu ₃)	2077	2004	1743	1622	
Ni(CO) ₃ (P(p-C ₆ H ₄ OCH ₃) ₃)	2066	1987	1724	1595	
Ni(CO) ₃ (PMe ₃)	2069	1994	1729	1606	
Ni(CO) ₃ (SbEt ₃)	2067	1996	1726	1609	
Ni(CO) ₃ (SbPh ₃)	2074	2005	1737	1624	
Ni(CO) ₃ (BiEt ₃)	2072	1996	1734	1609	

$$K(a_1) = 0.7477 \times K(e) + 528.17$$

(9 data points, R² = 0.9811)

2 Tricarbonyls

2.1 C_s Fe(CO)₃(diene) complexes

As is explained in the main text, Fe(CO)₂(diene)(L) complexes are used to calculate EFFFs for Fe(CO)₃(diene) species

Table S2: Fe(CO)₂(diene)(L) (and diene-like) molecules used to calculate EFFFs for Fe(CO)₃(diene)					
Molecule	$\nu(a')$	$\nu(a'')$	$K(a')$	$K(a'')$	Ref.
Fe(CO) ₂ (C ₇ H ₅)(PEt ₃)	1978	1920	1581	1490	A. Reckziegel and M. Bigorgne, <i>J. Organometal. Chem.</i> , 3 (1965) 341-354
Fe(CO) ₂ (C ₇ H ₈)(PEt ₃)	1969	1913	1566	1478	
Fe(CO) ₂ (butadiene)(PEt ₃)	1980	1921	1584	1490	
Fe(CO) ₂ (C ₇ H ₈)(PPh ₃)	1974	1921	1574	1490	
Fe(CO) ₂ (C ₇ H ₅)(P(OMe) ₃)	1993	1936	1604	1514	
Fe(CO) ₂ (C ₇ H ₈)(P(OMe) ₃)	1982	1928	1587	1501	
Fe(CO) ₂ (butadiene)(P(OMe) ₃)	1989	1934	1598	1511	

Fe(CO) ₂ (E-pentadiene)(P(OMe) ₃)	1989	1931	1598	1506	Gustorf & R. Rumlin <i>J. Organometal. Chem.</i> , 187 (1980) 361	
Fe(CO) ₂ (methylsorbate)(P(OMe) ₃)	2003	1946	1621	1530		
Fe(CO) ₂ (cyclobutadiene)(P(OMe) ₃)	1988	1932	1596	1508		
Fe(CO) ₂ (PhCHCHCOH)(PPh ₃)	2000	1947	1616	1531	G. Cardaci and G. Concetti, <i>J. Organometal. Chem.</i> , 90 (1974) 49-52	
Fe(CO) ₂ (PhCHCHCOH)(AsPh ₃)	2000	1951	1616	1538		
Fe(CO) ₂ (PhCHCHCOCH ₃)(PPh ₃)	2002	1947	1619	1531		
Fe(CO) ₂ (PhCHCHCOCH ₃)(SbPh ₃)	1997	1945	1611	1528		
Fe(CO) ₂ (PhCHCHCOPh)(PPh ₃)	2000	1947	1616	1531		
Fe(CO) ₂ (PhCHCHCOPh)(AsPh ₃)	2002	1947	1619	1531		
Fe(CO) ₂ (PhCHCHCOPh)(SbPh ₃)	2000	1947	1616	1531		
Fe(CO) ₂ (butadiene)(PPh ₃)	1973	1910	1572	1474		F. M. Chaudhari and P. L. Pauson, <i>J. Organometal. Chem.</i> , 5 (1966) 73-78
Fe(CO) ₂ (cyclohexadiene)(PPh ₃)	1960	1894	1552	1449		
Fe(CO) ₂ (cycloheptaadiene)(PPh ₃)	1965	1905	1560	1466		
Fe(CO) ₂ (cycloheptatriene)(PPh ₃)	1973	1920	1572	1489		
Fe(CO) ₂ (C ₄ Ph ₄)(PPh ₃)	1955	1904	1544	1464		
Fe(CO) ₂ (bda)(PPh ₃)	1999	1939	1614	1519	B. F. G. Johnson, J. Lewis, G. R. Stephenson and E. J. S. Vichi <i>J. C. S. Dalton</i> , 1978, 369-373	
Fe(CO) ₂ (bda)(P(OPh) ₃)	2015	1958	1640	1549		
Fe(CO) ₂ (cyclohexadiene)(PPh ₃)	1981	1927	1585	1500		
Fe(CO) ₂ (cyclohexadiene)(P(OPh) ₃)	2067	2021	1726	1650		
Fe(CO) ₂ (chd)(PPh ₃)	1979	1925	1582	1497		
Fe(CO) ₂ (chd)(P(OPh) ₃)	2065	2019	1722	1647		
Fe(CO) ₂ (MeO-chd)(PPh ₃)	1978	1924	1580	1495		
Fe(CO) ₂ (MeO-chd)(P(OPh) ₃)	2065	2018	1722	1645		
Fe(CO) ₂ (acetylgosterol)(PPh ₃)	1974	1920	1574	1489		

$$K(a') = 0.9191 \times K(a'') + 209.9$$

(31 data points, R² = 0.9884)

2.2 *fac*-Re(CO)₃(N-N)(ligand) complexes

As with the iron-diene dicarbonyls above, *fac*-Re(CO)₂(N-N)(X)(L) and [*fac*-Re(CO)₂(N-N)(L)(L')]⁺ are used to calculate EFFFs for *fac*-Re(CO)₃(N-N)(X) and [*fac*-Re(CO)₃(N-N)(L)]⁺, given as Table S3.

Table S3: <i>cis,trans</i> -Re(CO) ₂ (N-N)(L)(X) and [<i>cis,trans</i> -Re(CO) ₂ (N-N)(L)(L')] ⁺ molecules used to calculate EFFFs for <i>fac</i> -Re(CO) ₃ (N-N)(X) and [<i>fac</i> -Re(CO) ₃ (N-N)(L)] ⁺					
Molecule	$\nu(a')$	$\nu(a'')$	$K(a')$	$K(a'')$	Ref.
[Re(CO) ₂ (bpy)(c-dppene)] ⁺	1959	1888	1440	1550	J. L. Smithback, J. B. Helms, E. Schutte, S. M. Woessner, B. P. Sullivan <i>Inorg. Chem.</i> , 45 (2006) 2163-2174
[Re(CO) ₂ (bpy)(diphos)] ⁺	1952	1881	1429	1539	
[Re(CO) ₂ (bpy)(dppm)] ⁺	1950	1884	1434	1536	
Re(CO) ₂ (bpy)(MeCN)(Cl)	1909	1832	1356	1472	
[Re(CO) ₂ (bpy)(MeCN)(py)] ⁺	1937	1863	1402	1516	
[Re(CO) ₂ (bpy)(MeCN) ₂] ⁺	1928	1854	1388	1501	
[Re(CO) ₂ (bpy)(P(OCH ₃)Ph ₂) ₂] ⁺	1949	1879	1426	1534	
[Re(CO) ₂ (bpy)(P(OMe) ₂ Ph) ₂] ⁺	1957	1886	1437	1547	
[Re(CO) ₂ (bpy)(P(OMe) ₃) ₂] ⁺	1961	1888	1440	1553	
[Re(CO) ₂ (bpy)(PPh ₃) ₂] ⁺	1938	1868	1409	1517	
[Re(CO) ₂ (bpy)(PPh ₃) ₂] ⁺	1938	1868	1409	1517	
[Re(CO) ₂ (bpy) ₂] ⁺	1922	1852	1385	1492	
[Re(CO) ₂ (byp)(P(OPh) ₃) ₂] ⁺	1985	1914	1480	1592	
[Re(CO) ₂ (c-dppene)(PPh ₃)(bpy)] ⁺	1956	1886	1437	1545	
[Re(CO) ₂ (c-dppene)(PPh ₃)(phen)] ⁺	1960	1890	1443	1552	
[Re(CO) ₂ (dmbpy)(P(O-i-Pr) ₃) ₂] ⁺	1946	1871	1414	1530	
[Re(CO) ₂ (dmbpy)(P(p-FPh) ₃) ₂] ⁺	1939	1869	1411	1519	
[Re(CO) ₂ (dmbpy)(PPh ₃) ₂] ⁺	1936	1865	1405	1514	
[Re(CO) ₂ (dppm)(bpy)] ⁺	1950	1884	1434	1536	
[Re(CO) ₂ (dppm) ₂ (bpy)] ⁺	1940	1869	1411	1520	
[Re(CO) ₂ (Ph ₂ phen)(c-dppene)] ⁺	1958	1889	1441	1549	

[Re(CO) ₂ (Ph ₂ phen)(dppm)] ⁺	1949	1883	1432	1534	
[Re(CO) ₂ (phen)(c-dppene)] ⁺	1959	1889	1441	1550	
[Re(CO) ₂ (phen)(P(OPh) ₃) ₂] ⁺	1984	1914	1480	1590	
[Re(CO) ₂ (phen) ₂] ⁺	1922	1853	1387	1492	
[Re(CO) ₂ (t-dppene) ₂ (bpy)] ⁺	1942	1873	1417	1523	
Re(CO) ₂ (deeb)(Cl)(PMe ₃)	1920	1848	1379	1489	D. K. Kurtz, K. R. Brereton, K. P. Rufft, H. M. Tang, G. A.
[Re(CO) ₂ (deeb)(MeCN)(PMe ₃)] ⁺	1943	1873	1417	1525	N. Felton, A. J. M. Miller and J. L. Dempsey <i>Inorg. Chem.</i> , 57 (2018) 5389-5399
[Re(CO) ₂ (bpy)(P(OEt) ₃)(MeCN)] ⁺	1954	1878	1425	1542	K. Koike, J. Tanabe, S. Toyama, H. Tsubaki, K. Sakamoto,
[Re(CO) ₂ (bpy)(P(OEt) ₃)(py)] ⁺	1945	1871	1414	1528	J. R. Westwell, F. P. A. Johnson, H. Hori, H Saitoh and O. Ishitani,
[Re(CO) ₂ (bpy)(P(OEt) ₃)(PPh ₃)] ⁺	1948	1876	1422	1533	<i>Inorg. Chem.</i> , 39 (2000) 2777-2783
[Re(CO) ₂ (bpy)(P(OEt) ₃) ₂] ⁺	1956	1881	1429	1545	
[Re(CO) ₂ (bpy)(P(OEt) ₃)Cl]	1936	1857	1393	1514	
[Re(CO) ₂ (bpy)(PPh ₃)(MeCN)] ⁺	1944	1872	1416	1527	
[Re(CO) ₂ (bpy)(PPh ₃) ₂] ⁺	1938	1867	1408	1517	
[Re(CO) ₂ (Me ₂ bpy)(P(OEt) ₃)(PPh ₃)] ⁺	1946	1873	1417	1530	
[Re(CO) ₂ (Me ₂ bpy)(P(OEt) ₃)(PPh ₃)] ⁺	1944	1865	1405	1527	
[Re(CO) ₂ (Me ₂ bpy)(P(OEt) ₃) ₂] ⁺	1954	1879	1426	1542	
[Re(CO) ₂ ((CF ₃) ₂ bpy)(P(OEt) ₃) ₂] ⁺	1963	1891	1444	1556	
[Re(CO) ₂ (bpy)(P(OEt) ₃) ₂] ⁺ (Br ⁻ /CH ₂ Cl ₂)	1956	1882	1431	1545	O. Ishitani, M. W. George, T. Ibusuki, F. P. A. Johnson, K. Koike, K. Nozaki, C. Pac, J. J. Turner and J. R. Westwell,
[Re(CO) ₂ (bpy)(P(OEt) ₃) ₂] ⁺ (Br ⁻ /CH ₃ CN)	1956	1881	1429	1545	<i>Inorg. Chem.</i> , 33 (1994) 4712-4717
[Re(CO) ₂ (bpy)(P(OEt) ₃) ₂] ⁺ (Br ⁻ /DMF)	1953	1879	1426	1541	
[Re(CO) ₂ (bpy)(P(OEt) ₃) ₂] ⁺ ([BPh ₄] ⁻ /CH ₂ Cl ₂)	1957	1884	1434	1547	
[Re(CO) ₂ (bpy)(P(OEt) ₃) ₂] ⁺ ([BPh ₄] ⁻ /CH ₃ CN)	1955	1881	1429	1544	

[Re(CO) ₂ (bpy)(P(OEt) ₃) ₂] ⁺ ([BPh ₄] ⁻ /DMF)	1953	1879	1426	1541	
[Re(CO) ₂ (dmbpy)(P(MeOPh) ₃) ₂] ⁺	1902	1825	1345	1461	H. Tsubaki, A. Sekine, Y. Ohashi, K. Koike, H. Takeda and O. Ishitani <i>J. Am. Chem. Soc.</i> , 127 (2005) 15544-15555
[Re(CO) ₂ (dmbpy)(P(MeOPh) ₃) ₂]	1930	1859	1396	1505	
[Re(CO) ₂ (dmbpy)(P(MeOPh)(PPh ₃)) ⁺	1933	1861	1399	1509	
[Re(CO) ₂ (dmbpy)(PPh ₃) ₂]	1908	1830	1353	1470	
[Re(CO) ₂ (dmbpy)(PPh ₃) ₂] ⁺	1936	1865	1405	1514	
[Re(CO) ₂ (dmbpy)(P(FPh) ₃ (PPh ₃)) ⁺	1937	1867	1408	1516	
[Re(CO) ₂ (dmbpy)(P(FPh) ₃) ₂]	1910	1834	1359	1474	
[Re(CO) ₂ (dmbpy)(P(FPh) ₃) ₂] ⁺	1939	1869	1411	1519	
[Re(CO) ₂ (dmbpy)(P(ClPh) ₃) ₂]	1912	1837	1363	1477	
[Re(CO) ₂ (dmbpy)(P(ClPh) ₃) ₂] ⁺	1942	1872	1416	1523	
[Re(CO) ₂ (dmpy)(P(MeOPh) ₃ (P(OPr) ₃)) ⁺	1939	1865	1405	1519	
[Re(CO) ₂ (dmbpy)(PPh ₃)(P(OEt) ₃)]	1917	1840	1368	1484	
[Re(CO) ₂ (dmbpy)(PPh ₃)(P(OEt) ₃) ⁺	1945	1872	1416	1528	
[Re(CO) ₂ (dmbpy)(P(OPr) ₃) ₂]	1919	1840	1368	1487	
[Re(CO) ₂ (dmbpy)(P(OPr) ₃) ₂] ⁺	1946	1871	1414	1530	
[Re(CO) ₂ (dmbpy)(POEt) ₃) ₂] ⁺	1953	1879	1426	1541	
[Re(CO) ₂ (dmbpy)(P(OEt) ₃)(P(OMe) ₃) ⁺	1956	1882	1431	1545	

$$K(a') = 0.9525 \times K(a'') + 178.9$$

(62 data points; R² = 0.9748)

2.3 *mer* – M(CO)₃L₃ complexes (M = Cr, Mo, W)

For these species the ideal data would be obtained from *trans* – M(CO)₂L₄ molecules, but unfortunately, such information is sparse, so it is necessary to proceed in a roundabout way. The EFFF constants for a range of M(CO)₅L have been obtained *via* isotopic substitution: $k_{ax}, k_{eq}, k_{ax,eq}, k_{eq,eq}^{cis}, k_{eq,eq}^{trans}$. Assuming that for a set of theoretical *trans*-M(CO)₂L₄ molecules, we can use k_{eq} and $k_{eq,eq}^{trans}$ it becomes possible to predict the $K(a_1)$ and $K(b_2)$ values for these hypothetical dicarbonyls. Table S4 shows the calculation of these values

Table S4: $M(CO)_5L$ molecules used to calculate the $K(a_1)$ and $K(b_2)$ values of the theoretical $trans-M(CO)_2L_4$ species en route to $mer-M(CO)_3L_3$ systems			
Molecule	$K(a_1)$	$K(b_1)$	Ref.
$Mo(CO)_5(PPh_3)$	1655	1537	D. J. Darensbourg and M. A. Murphy, <i>J. Am. Chem. Soc.</i> , 100 (1978) 463-468
$Cr(CO)_6$ ($^{13}C^{18}O$ CH_4 20K)	1699	1593	J. A. Timney <i>PhD Thesis, Newcastle University</i> 1980
$Cr(CO)_6$ (^{13}CO CH_4 20K)	1696	1592	R. N. Perutz and J. J. Turner <i>Inorg. Chem.</i> , 14 (1975) 262-270
$Cr(CO)_6$ (^{13}CO Ar 20K)	1702	1598	
$Cr(CO)_6$ (^{13}CO cyclohexane)	1695	1592	
$Cr(CO)_6$ (^{13}CO alkane)	1700	1592	
$Mo(CO)_6$ (^{13}CO CH_4 20K)	1700	1594	
$W(CO)_6$ (^{13}CO CH_4 20K)	1693	1585	
$Cr(CO)_5(CS)$	1724	1631	M. Poliakoff <i>Inorg. Chem.</i> , 15 (1976) 2022-2031
$Cr(CO)_5(NHC_5H_{10})$	1642	1510	D. J. Darensbourg and M. A. Murphy, <i>Inorg. Chem.</i> , 17 (1978) 884-888
$Cr(CO)_5(H_2)$	1689	1575	R. K. Upmacis, M. Poliakoff and J. J. Turner <i>J. Am. Chem. Soc.</i> , 108 (1986) 3645-3651
$Mo(CO)_5(H_2)$	1694	1581	
$W(CO)_5(H_2)$	1684	1571	
$Cr(CO)_5$ (^{13}CO CH_4 20K)	1674	1554	R. N. Perutz and J. J. Turner <i>Inorg. Chem.</i> , 14 (1975) 262-270
$Cr(CO)_5$ (^{13}CO Ar 20K)	1681	1561	
$Mo(CO)_5$ (^{13}CO CH_4 20K)	1681	1563	
$W(CO)_5$ (^{13}CO CH_4 20K)	1671	1547	
$Mo(CO)_5(N_2)$ 1	1692	1580	J. K. Burdett, A. J. Downs, G. P. Gaskill, M. A. Graham, J. J. Turner and R. F. Turner <i>Inorg. Chem.</i> , 17 (1978) 523-532 The multiple values for $Mo(CO)_5(N_2)$ arise from the different ways the force constants were calculated.
$Mo(CO)_5(N_2)$ 2	1687	1580	
$Mo(CO)_5(N_2)$ 3	1689	1581	
$Mo(CO)_5(N_2)$ 4	1691	1581	

$$K(a_1) = 0.6771 \times K(b_2) + 620.5$$

(21 data points, $R^2 = 0.9804$)

3 Tetracarbonyls

3.1 *cis*-M(CO)₄L₂ complexes (M = Cr, Mo, W)

There are two approaches (the b_2 method and the b_1 method) to finding EFFF force constants for these molecules.

The secular equations for these molecules are:

$$a_1: \begin{vmatrix} k_1 + k_{11} - K & 2k_{12} \\ 2k_{12} & k_2 - K \end{vmatrix} = 0$$

$$b_1: K(b_1) = k_1 - k_{11}$$

$$b_2: K(b_2) = k_2 - k_{22}$$

We start with data for $K(a_1)$ and $K(b_2)$ for *cis*-M(CO)₂(L)₄ complexes (M = Cr, Mo, W). (Table S5a). This is rather limited but we can also use the isotopic data for M(CO)₅L systems, as for the *mer*-M(CO)₃L₃, but this time calculate the theoretical *cis*-M(CO)₂L₄ $K(a_1)$ and $K(b_2)$ data. These calculations are shown in Table S5b. In fact, there was no statistical difference between the results for the two approaches, and the 32 data points give an excellent straight-line plot

$$K(a_1) = 0.8507 \times K(b_2) + 296.7$$

(32 data points, $R^2 = 0.9981$)

Table S5a: <i>cis</i> -M(CO) ₂ (L) ₄ (M = Cr, Mo, W) molecules used to calculate EFFFs for <i>cis</i> -M(CO) ₄ (L) ₂ (using the b_2 mode)					
Molecule	$\nu(a_1)$	$\nu(b_2)$	$K(a_1)$	$K(b_2)$	Ref.
Mo(CO) ₂ (PF ₃) ₄	2048	2010	1694	1632	P. S. Braterman, "Metal Carbonyl Spectra" Table 7.13 (p206) and references therein
Mo(CO) ₂ (P(OMe) ₃) ₄	1909	1856	1472	1391	
Cr(CO) ₂ (phen)(P(OEt) ₃) ₂	1827	1743	1348	1227	
Mo(CO) ₂ (phen)(P(OEt) ₃) ₂	1872	1790	1416	1294	
W(CO) ₂ (phen)(P(OEt) ₃) ₂	1825	1740	1345	1223	
Mo(CO) ₂ (dppe) ₂	1850	1783	1382	1284	J. R. Sowa, J. B. Bonanno, V. Zanotti, and R. J. Angelici <i>Inorg. Chem.</i> 31 (1992) 1370-1375
Mo(CO) ₂ (dppp) ₂	1857	1790	1393	1294	
Mo(CO) ₂ (arphos) ₂	1848	1778	1379	1277	
Mo(CO) ₂ (dmpe) ₂	1836	1766	1362	1260	
W(CO) ₂ (dppe) ₂	1851	1781	1384	1281	
Mo(CO) ₂ (diars) ₂	1887	1828	1438	1350	

Table S5b: Hypothetical <i>cis</i>-M(CO)₂(L)₄ (M = Cr, Mo, W) molecules calculated from isotopic data used to calculate EFFFs for <i>cis</i>-M(CO)₄(L)₂ (using the <i>b</i>₂ mode)			
Molecule	<i>K</i> (<i>a</i> ₁)	<i>K</i> (<i>b</i> ₂)	Ref.
Mo(CO) ₅ (PPh ₃)	1628	1564	D. J. Darensbourg and M. A. Murphy, <i>J. Am. Chem. Soc.</i> , 100 (1978) 463-468
Cr(CO) ₆ (¹³ C ¹⁸ O CH ₄ 20K)	1672	1619	J. A. Timney <i>PhD Thesis, Newcastle University 1980</i>
Cr(CO) ₆ (¹³ CO CH ₄ 20K)	1671	1618	R. N. Perutz and J. J. Turner <i>Inorg. Chem.</i> , 14 (1975) 262-270
Cr(CO) ₆ (¹³ CO Ar 20K)	1676	1624	
Cr(CO) ₆ (¹³ CO cyclohexane)	1669	1617	
Cr(CO) ₆ (¹³ CO alkane)	1672	1620	
Mo(CO) ₆ (¹³ CO CH ₄ 20K)	1675	1619	
W(CO) ₆ (¹³ CO CH ₄ 20K)	1669	1609	
Cr(CO) ₅ (CS)	1701	1654	M. Poliakoff <i>Inorg. Chem.</i> , 15 (1976) 2022-2031
Cr(CO) ₅ (NHC ₅ H ₁₀)	1606	1546	D. J. Darensbourg and M. A. Murphy, <i>Inorg. Chem.</i> , 17 (1978) 884-888
Cr(CO) ₅ (H ₂)	1661	1603	R. K. Upmacis, M. Poliakoff and J. J. Turner <i>J. Am. Chem. Soc.</i> , 108 (1986) 3645-3651
Mo(CO) ₅ (H ₂)	1668	1608	
W(CO) ₅ (H ₂)	1659	1596	
Cr(CO) ₅ (¹³ CO CH ₄ 20K)	1644	1583	R. N. Perutz and J. J. Turner <i>Inorg. Chem.</i> , 14 (1975) 262-270
Cr(CO) ₅ (¹³ CO Ar 20K)	1652	1591	
Mo(CO) ₅ (¹³ CO CH ₄ 20K)	1653	1590	
W(CO) ₅ (¹³ CO CH ₄ 20K)	1643	1575	
Mo(CO) ₅ (N ₂) 1	1665	1607	J. K. Burdett, A. J. Downs, G. P. Gaskill, M. A. Graham, J. J. Turner and R. F. Turner <i>Inorg. Chem.</i> , 17 (1978) 523-532
Mo(CO) ₅ (N ₂) 2	1660	1608	
Mo(CO) ₅ (N ₂) 3	1662	1608	

Mo(CO) ₅ (N ₂) ₄	1663	1608	
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We can now use the two methods to predict values for M(CO)₄L₂

3.1.1 The *b*₂ method

We need **two** of the CO groups in *cis*-M(CO)₄(L)₂ to be silenced this time, giving *cis*-M(CO)₂(CO)₂(L)₂. The *b*₂ mode of this molecule is identical to the *b*₂ mode in the *cis*-M(CO)₂(L)₄ complex so we can calculate a $K(\underline{a}_1)$ for this molecule and thus the force constants for the equatorial CO groups.

$$k_2 = \frac{1}{2}(K(\underline{a}_1) + K(b_2)) \qquad k_{22} = \frac{1}{2}(K(\underline{a}_1) - K(b_2))$$

Having *k*₂ and *k*₂₂ we can now calculate the remaining three force constants in *cis*-M(CO)₄(L)₂.

$$k_1 = [K(a_1)_1 + K(a_1)_2 + K(b_1) + K(b_2) - 2k_2]/2 \qquad k_{11} = k_1 - K(b_1)$$

$$k_{12} = \sqrt{\frac{[k_1 + k_{11} - K(a_1)_1][k_2 + k_{22} - K(a_1)_1]}{4}}$$

3.1.2 The *b*₁ method

This second approach is only slightly different to the *b*₂ method. We need to start with molecules of the general formula *trans*-M(CO)₂(L)₄. Unfortunately, the experimental data for such complexes is lacking so we use the same data we used in the case of *mer*-M(CO)₃(L)₃ (Table S4). These give the force constants for the *a*₁ and *b*₁ modes of the hypothetical molecules *trans*-M(CO)₂(CO)₃(L) where the two vibrating CO groups are *trans* to one another (and there are three non-vibrating, “silent” CO groups). So, starting with the *b*₁ mode in *cis*-M(CO)₄(L)₂, and again silencing two of the CO groups, the **reference line** is:

$$K(\underline{a}_1) = 0.6771 \times K(b_1) + 620.5 \quad (\text{the same as for } mer\text{-M(CO)}_3\text{(L)}_3 \text{ complexes})$$

and the procedure is identical only this time *k*₁ and *k*₁₁ are calculated first.

The *cis*-M(CO)₄(L)₂ carbonyls are a good test of the silent CO method and the force constants calculated using the *b*₂ method and the *b*₁ method are reassuringly close. The case of W(CO)₄(diphos) is highlighted in the main text.

3.2 C_{3v} and C_{2v} Fe(CO)₄L complexes

3.2.1 C_{3v} symmetry Fe(CO)₄(L) where L is axial

A large number of ligands replace an *axial*-CO group in Fe(CO)₅ to produce the C_{3v} isomer of Fe(CO)₄(L). The same is true of the corresponding ruthenium and osmium complexes. This configuration, yet again, has an underdetermined force field with three frequencies ($2a_1 + e$) and four force constants (k_1, k_2, k_{11}, k_{12}).

The secular equations are:

$$a_1: \begin{vmatrix} k_1 + 2k_{11} - K & \sqrt{3}k_{12} \\ \sqrt{3}k_{12} & k_2 - K \end{vmatrix} = 0$$

$$e: K(e) = k_1 - k_{11}$$

The reference line for this class of compounds would ideally have originated from data from *trans*-M(CO)₃(L)₂ or *trans*-M(CO)₃(L)(L') species and M(CO)₂(L)₃ complexes (M = Fe, Ru, Os) with all CO groups in equatorial positions.

So once again we resort to isotopic data, this time for axially-substituted Fe(CO)₄(phosphine) and equatorially-substituted Fe(CO)₄(olefin) complexes. Employing the k_1 and k_{11} (k_{eq} and $k_{eq,eq}$) numbers permits prediction of the two frequencies, and hence K values, for the theoretical C_{2v} Fe(CO)₂L₃ systems. These numbers are given in Table S6.

This produces a reference line:

$$K(a_1) = 0.8076 \times K(e) + 387.3$$

(13 points, R² = 0.9946)

Table S6: Hypothetical C _{2v} -Fe(CO) ₂ (L) ₄ data calculated from isotopic data			
Molecule	K(a ₁)	K(e)	Ref.
Fe(CO) ₅	1697	1617	G. Bor <i>Inorg. Chim. Acta</i> , 3 (1969) 191-195
Fe(CO) ₂ (PF ₃) ₃ [C _{2v} isomer]	1679	1595	R. J. Clark <i>Inorg. Chem.</i> , 3 (1964) 1395-1398
Fe(CO) ₄ (PPh ₃)	1616	1526	D. J. Darensbourg, H. H. Nelson and C. L. Hyde <i>Inorg. Chem.</i> , 13 (1975) 2135-2145
Fe(CO) ₄ (PPhMe ₂)	1610	1516	
Fe(CO) ₄ (P(OPh) ₃)	1637	1547	
Fe(CO) ₄ (P(OMe) ₃)	1634	1542	
Fe(CO) ₄ (PPh ₂ OMe)	1625	1531	
Fe(CO) ₄ (P <i>n</i> -Bu ₃)	1607	1509	
Fe(CO) ₄ (CH ₂ =CHCOCl)	1666	1734	
Fe(CO) ₄ (CH ₂ =CHCOOH)	1655	1715	
Fe(CO) ₄ (CH ₂ =CHCONC ₅ H ₁₀)	1629	1701	
Fe(CO) ₄ (CH ₂ =CHCN)	1664	1732	

Fe(CO) ₅	1695	1615	P. Portius, M. Bühl, M. W. George, F-W Grevels and James J. Turner <i>Organometallics</i> , 38 (2019) 4288–4297
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This reference line allows us to calculate the force constants in a C_{3v} tetracarbonyl by making $K(b_2) = K(e)$ and calculating a value for $K(\underline{a}_1)$ (as before) so the force constants are:

$$k_1 = \frac{1}{2}(K(\underline{a}_1) + K(e))$$

$$k_{11} = \frac{1}{2}(K(\underline{a}_1) - K(e))$$

$$k_2 = K(a_1)_1 + K(a_1)_2 + 2K(e) - 3k_1$$

$$k_{12} = \sqrt{\frac{[k_1 + 2k_{11} - K(a_1)_1][k_2 - K(a_1)_1]}{3}}$$

3.2.2 C_{2v} symmetry Fe(CO)₄(L) where L is equatorial

There are fewer M(CO)₄(L) (M = Fe) complexes with a C_{2v} geometry although that number increases when the metal atom is Ru or Os. The secular equations for these molecules are identical to the C_{2v} molecules based on an octahedron with the sole difference that the reference line is the same as was used for the C_{3v} tetracarbonyls above (section 3.2.1) since the b_2 mode of a C_{2v} Fe(CO)₄(L) species is identical in form to the e mode of the C_{3v} tetracarbonyl. This enables us, as an example, to calculate the force constants of Fe(CO)₄(CS) (data from W. Petz, *J. Organomet. Chem.* 146 (1978) C23-25) and they are shown, for comparison, alongside Fe(CO)₅ (for which we have force constants from isotopic data).

Force constants for Fe(CO)₄(CS) and Fe(CO)₅

Molecule	k_1	k_2	k_{11}	k_{12}	k_{22}
Fe(CO) ₄ (CS) [using b_2 mode]	1654	1717	38	21	45
Fe(CO) ₅ [from Bor]	1657	1695	41	28	40

4 Pentacarbonyls

4.1 C_{4v} M(CO)₅(L) complexes (M = Cr, Mo, W) and M(CO)₅(X) (M = Mn, Re)

There have been many force field studies (both approximate and from isotopic data) on the M(CO)₅(L) complexes (M = Cr, Mo, W) and a significant but smaller number on M(CO)₅(X) (M = Mn, Re) compounds. It was with this type of molecule that the CO-factored force field first came to be used in the 1960's. There are five force constants in the EFFF but only four possible $\nu(CO)$ absorptions ($2a_1 + b_2 + e$). The b_2 mode is formally Raman-active only and is often either missing or a weak, broader absorption. It has been argued that the presence in the infrared spectrum of the b_2 mode implies distortion in the molecule away from C_{4v} symmetry to C_s (with $3a' + 2a''$ modes) and a more complicated force field. Braterman commented that, unless the ligand L possessed a four-fold axis of symmetry, the maximum possible molecular symmetry is C_s and the " b_2 " mode becomes allowed, although still with a low relative intensity. The force field of a C_s pentacarbonyl has eight force constants (

$k_1, k_2, k_3, k_{11}, k_{22}, k_{12}, k_{13}, k_{23}$) and whilst some approximations realistically might be made (e.g. $k_{11} \approx k_{22}, k_{13} \approx k_{23}$) there are still three degrees of freedom.

Assuming C_{4v} symmetry, if the b_2 mode is observed the force field is underdetermined with one degree of freedom, but the symmetry may be, as we have seen, effectively lower. If the b_2 mode is not observed there are two degrees of freedom. Cotton's approach for the first of these scenarios was to set the *cis* interaction constant (between equatorial CO groups) equal to half the *trans* interaction constant. To cope with the second scenario, k_{12} was also set equal to the *cis* interaction constant, that is (in the notation used throughout this paper):

$$k_{11}^c = \frac{1}{2}k_{11}^t = k_{12}$$

This limitation is unnecessary with the silent-CO method.

The secular equations linking EFFF force constants with symmetry force constants are:

$$a_1: \begin{vmatrix} k_1 + k_{11}^t + 2k_{11}^c - K & 2k_{12} \\ 2k_{12} & k_2 - K \end{vmatrix} = 0$$

$$b_2: K(b_2) = k_1 - 2k_{11}^c + k_{11}^t$$

$$e: K(e) = k_1 - k_{11}^t$$

We shall treat the Group 6 metal carbonyls and Group 7 metal carbonyls separately.

4.1.1 $M(CO)_5(L)$ ($M = Cr, Mo, W$)

The reference line for $M(CO)_5(L)$ ($M = Cr, Mo, W$) is exactly the same as for *mer*- $M(CO)_3(L)_3$ complexes and refers to the hypothetical $M(CO)_2(\underline{CO})_3(L)$ molecule where the vibrating CO groups are mutually *trans*. So we use $K(\underline{a}_1)$ to represent the symmetric stretch of this *trans*-dicarbonyl and $K(e)$ from the parent pentacarbonyl).

$$K(\underline{a}_1) = 0.6771 \times K(e) + 620.5$$

This enables us to calculate k_1 and k_{11}^t as though $M(CO)_5(L)$ was a *trans*-dicarbonyl; $M(CO)_2(\underline{CO})_3(L)$.

$$k_1 = \frac{1}{2}(K(\underline{a}_1) + K(e)) \qquad k_{11}^t = \frac{1}{2}(K(\underline{a}_1) - K(e))$$

This removes one degree of freedom but if the b_2 mode is not observed the force field is still underdetermined as $K(b_2)$ cannot be calculated. However, the e mode and b_2 mode of $M(CO)_5(L)$ only involve the motion of the equatorial CO groups, with no complicating contribution from the axial CO group so we might expect a strong correlation between $K(b_2)$ and $K(e)$, using the force constants from the $M(CO)_5(L)$ complexes that have had a full EFFF determined. This is exactly what we find:

$$K(b_2) = 0.8492 \times K(e) + 291.9 \quad (18 \text{ data points } R^2 = 0.9863)$$

So, regardless of whether the b_2 mode is observed or not, the force constants can be calculated.

$$k_2 = K(a_1)_1 + K(a_1)_2 + K(b_2) + 2K(e) - 4k_1$$

$$k_{11}^c = \frac{1}{2}(k_1 + k_{11}^t - K(b_2))$$

$$k_{12} = \sqrt{\frac{[k_1 + 2k_{11}^c + k_{11}^t - K(a_1)_1][k_2 - K(a_1)_1]}{4}}$$

4.1.2 Mn(CO)₅(X)

The Group 7 metals (Mn, Tc, Re) can, in theory, be treated the same way although there are far fewer force fields calculated from isotopic spectra available and consequently there is less confidence in the reference lines. The only metal where enough data exists is Mn.

To date, only Mn(CO)_{5-x}(¹³CO)_xH, Mn(CO)_{5-x}(¹³CO)_xCl and (in a CO matrix) Mn(CO)₅ have been studied where the full range of substituted molecules were used to determine force constants. Earlier work by Kaesz *et al* used less ¹³CO substitution but, nonetheless, a robust set of force constants were produced for each of the M(CO)₅X molecules (M = Mn, Re; X = Cl, Br, I). Using the same reference line as the chromium group produces poor agreement. However, using the limited number of studies available gives a reference line for Mn compounds with two CO groups *trans* (*i.e.* *trans*-Mn(CO)₂(CO)₃(X)) to each other:

$$K(a_1) = 0.8201 \times K(e) + 350.1 \quad (9 \text{ data points, } R^2 = 0.9882)$$

This is significantly different from that used for the Group 6 compounds. Using the same data we can also produce an analogous relationship between the $K(b_2)$ and $K(e)$ symmetry force constants.

$$K(b_2) = 1.0178 \times K(e) + 18.5 \quad (7 \text{ data points, } R^2 = 0.9989)$$

Again, this is very different from the equation used for Group 6 complexes, but the amount of data is limited. There are not enough data to produce similar relationships for Re(CO)₅X nor Tc(CO)₅(X) complexes.

Table S7: <i>trans</i> -Mn(CO) ₂ (<u>CO</u>) ₃ (X) molecules to calculate EFFFs for Mn(CO) ₅ (X).			
Molecule	$K(a')$	$K(a'')$	Ref.
Mn(CO) ₅ Cl	1796	1706	H. D. Kaesz, R. Bau, D. Hendrickson and J. M. Smith <i>J. Am. Chem. Soc.</i> , 89 (1967) 2844-2851
Mn(CO) ₅ Br	1784	1698	

Mn(CO) ₅ I	1771	1687	
Mn(CO) ₅ CH ₃	1728	1634	
Mn(CO) ₅ H (CH ₄ , 20K)	1739	1643	S. P. Church, M. Poliakoff, J. A. Timney and J. J. Turner <i>Inorg. Chem.</i> , 22 (1983) 3259-3266
Mn(CO) ₅ Cl (CH ₄ , 12K)	1803	1710	T. McHugh, A. J. Rest and D. J. Taylor <i>J. C. S. Dalton</i> , (1980) 1803-1808
Mn(CO) ₅ (CO, 20K)	1706	1596	S. P. Church, M. Poliakoff, J. A. Timney and J. J. Turner <i>J. Am. Chem. Soc.</i> , 103 (1981) 7515-7520
Mn(CO) ₅ H	1736	1640	P. S. Braterman, R. W. Harrill and H. D. Kaesz <i>J. Am. Chem. Soc.</i> , 89 (1967) 2851-2855
Mn(CO) ₅ D	1737	1640	

5 Force Constant Calculations for Fe(CO)₄(N₂)

The characterization of Fe(CO)₄(N₂) in a nitrogen matrix is an interesting application of the “silent-CO” method and we include additional information here that supports our conclusion that the molecule has a C_{3v} structure with the N₂ ligand occupying an axial position in the trigonal bipyramid.

The $\nu(NN)$ stretching region

The first hint of the correct structure comes from the value of the N-N stretching vibration. We showed, many years ago¹, that the NN force constant of M(L)_n(N₂) was linearly related to the force constant of the equivalent carbonyl M(L)_n(CO):

$$k_{NN}[M(L)_n(N_2)] = 1.355k_{CO}[M(L)_n(CO)] - 210$$

So, for Fe(CO)₄(N₂), there are two possible $\nu(NN)$ frequencies because the equivalent carbonyl (Fe(CO)₅) has two chemically different CO groups. Recently, Portius, Turner² and colleagues have calculated the force constants for Fe(CO)₅ and this enables us to predict $k(NN)$ and thus $\nu(NN)$ for both likely isomers of Fe(CO)₄(N₂):

Observed $\nu(NN)$ (average)	2246 cm ⁻¹
Predicted $\nu(NN)$, structure A (C _{3v})	2251 cm ⁻¹
Predicted $\nu(NN)$, structure B (C _{2v})	2219 cm ⁻¹

Clearly, the predicted frequency (obsd - calc = -5 cm⁻¹) for A is much closer to the observed frequency than that predicted (obsd - calc = +27 cm⁻¹) for B. This gives the first strong indication that A is the correct structure.

We would note that the $\nu(NN)$ stretch of $\text{Fe}(\text{CO})_4(\text{N}_2)$ (either isomer; A or B) will be of symmetry a_1 so we would expect some mixing with the $\nu(\text{CO})$ stretches of the same symmetry. The magnitude of the interaction constant $k_{\text{CO},\text{NN}}$ is probably comparable to $k_{\text{CO},\text{CO}}$ but this, in fact, makes very little difference to the $\nu(\text{CO})$ and $\nu(\text{NN})$ frequencies; they are effectively decoupled.

Reference Lines for $\text{Fe}(\text{CO})_4(\text{L})$

The reference line for $\text{Fe}(\text{CO})_4(\text{L})$ is actually for $\text{Fe}(\text{CO})_2(\underline{\text{CO}})_2(\text{L})$ where the two vibrating CO groups are in the equatorial plane. This means that we use the same reference line for C_{3v} $\text{Fe}(\text{CO})_4(\text{L})$ and C_{2v} $\text{Fe}(\text{CO})_4(\text{L})$.

$$K(\underline{a}_1) = 0.8076 \times K(b_2) + 387.3$$

For C_{3v} $\text{Fe}(\text{CO})_4(\text{L})$ (where $K(e) = K(b_2)$)

$$k_1 = \frac{1}{2}[K(\underline{a}_1) + K(e)]$$

$$k_{11} = \frac{1}{2}[K(\underline{a}_1) - K(e)]$$

$$k_2 = K(a_1)_1 + K(a_1)_2 + 2K(e) - 3k_1$$

$$k_{12} = \sqrt{\frac{[k_1 + 2k_{11} - K(a_1)_1][k_2 - K(a_1)_1]}{3}}$$

This gives, for C_{3v} $\text{Fe}(\text{CO})_4(\text{N}_2)$:

$$k_1 = 1630 \quad k_2 = 1684 \quad k_{11} = 41 \quad k_{12} = 35$$

For C_{2v} $\text{Fe}(\text{CO})_4(\text{L})$

There are two modes we can apply the silent CO method to: b_2 (as with the C_{3v} isomer above) or, with less confidence, the b_1 (taking the reference line used for the octahedral $\text{M}(\text{CO})_4(\text{L})_2$ species) from two CO groups at 180°)

Using the b_2 mode:

This uses the same reference line as the C_{3v} isomer:

$$K(\underline{a}_1) = 0.8076 \times K(b_2) + 387.3$$

Thus:

$$k_1 = \frac{1}{2}[K(\underline{a}_1) + K(b_2)]$$

$$k_{11} = \frac{1}{2}[K(\underline{a}_1) - K(b_2)]$$

$$k_2 = \frac{1}{2} (K(a_1)_1 + K(a_1)_2 + K(b_1) + K(b_2) - 2k_1)$$

$$k_{12} = \sqrt{\frac{[k_1 + k_{11} - K(a_1)_1][k_2 + k_{22} - K(a_1)_1]}{4}}$$

Depending on the way the bands are assigned, this gives two solutions (see main text).

The C_{2v} $Fe(CO)_4(L)$ case has an alternative approach using a different reference line (i.e. that used in the octahedral $M(CO)_4(L)_2$ complexes) that applies to the b_1 mode rather than the b_2 :

$$K(\underline{a}_1) = 0.6771 \times K(b_1) + 621$$

$$k_2 = \frac{1}{2} [K(\underline{a}_1) + K(b_1)]$$

$$k_{22} = \frac{1}{2} [K(\underline{a}_1) - K(b_1)]$$

$$k_1 = \frac{1}{2} (K(a_1)_1 + K(a_1)_2 + K(b_1) + K(b_2) - 2k_2)$$

$$k_{12} = \sqrt{\frac{[k_1 + k_{11} - K(a_1)_1][k_2 + k_{22} - K(a_1)_1]}{4}}$$

If structure B was correct, we would expect at least one of the solutions from the different assignments to be close. [See table below] For all the C_{2v} $Fe(CO)_4(L)$ species (apart from " C_{2v} $Fe(CO)_4(N_2)$ ") examined thus far (in the main text $Fe(CO)_4(C_2H_4)$ was added as an example) there is very close agreement between the two methods.

Comparison of calculated force constants (Nm^{-1}) for C_{2v} $Fe(CO)_4(N_2)$ (**B**) using the b_1 mode and the b_2 mode and the reference lines as above.

Assig.	Mode	a_1	a_1	b_1	b_2	k_1	k_2	k_{11}	k_{22}	k_{12}
1	b_2	2083.3	1981.6	2006.8	1971.7	1613	1655	43	29	41
	b_1	2083.3	1981.6	2006.8	1971.7	1593	1674	24	48	33
2	b_2	2083.3	1981.6	1971.7	2006.8	1664	1604	37	34	39
	b_1	2083.3	1981.6	1971.7	2006.8	1641	1626	15	57	41

As a check of the method, we used the known C_{2v} structure of $Fe(CO)_4(C_2H_4)$, which has an equatorial C_2H_4 , as this gives a comparable molecule to show how the "silent CO" method *should* work. This molecule has $\nu(CO)$ frequencies at 2087, 2013 (sh),

2007, 1984 cm^{-1} with the 2007 cm^{-1} band being the most intense³. The force constants can be calculated by using the b_1 mode or the b_2 mode as a starting point. The results are given in Table S8:

Table S8:
Calculated EFFF force constants (in Nm^{-1}) for $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$

	k_1	k_2	k_{11}	k_{22}	k_{12}
Using b_1 mode	1631	1676	41	49	28
Using b_2 mode	1632	1674	42	48	28

The agreement between the two calculations is extremely good; unlike for C_{2v} $\text{Fe}(\text{CO})_4(\text{N}_2)$

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- 1 J. A. Timney, *The Identification of Metal Carbonyl Fragments*, PhD Thesis, Newcastle University (1979)
 - 2 P. Portius, M. Buhl, M. W. George, F-W. Grevels and J. J. Turner, *Organometallics* 2019, **38**, 4288
 - 3 B. H. Weiller, M. E. Miller and Edward R. Grant, *J. Am. Chem. Soc.*, 1987, **109**, 352