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CORRELATIONS OF CARBONYL STRETCHING FREQUENCIES AND ^{31}P AND ^{95}Mo NMR PARAMETERS FOR *FAC*-[Mo(CO)$_3$(bipy)(PR$_3$)] COMPLEXES

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Abstract—Several complexes of the type [Mo(CO)$_3$(bipy)(PR$_3$)] [where bipy = 2,2′-dipyridine, R = *n*-Bu, Me, *p*-C$_6$H$_4$-X; X = F, Cl, H, CH$_3$, OCH$_3$, N(CH$_3$)$_2$] were synthesized and characterized by ^{31}P NMR, ^{95}Mo NMR and IR spectroscopy. Relationships are drawn between the bonding nature of the ligands and the ^{95}Mo and ^{31}P NMR chemical shifts and the ν(C≡O) values. Correlations of $\delta(^{95}\text{Mo})$, $\Delta\delta(^{31}\text{P})$ and ν(C≡O) to various parameters such as ligand pK_a, ligand cone angle (Θ), and the Kabachnik parameter ($\Sigma\sigma^{\phi}$) are discussed and indicate the interrelationship of the donor abilities of C≡O, dipy and the phosphine ligands. The importance of steric effects in influencing net metal electron density is demonstrated by the results.

IR data for the carbonyl region has been central to studies of the structural and electronic properties of transition metal carbonyl complexes for almost three decades.[1] Carbonyl stretching force constants were among the first parameters used to relate the σ-donor and π-acceptor ability of ligands in metal carbonyl complexes.[2] With the advent of Fourier transform NMR techniques, however, the bonding properties of ligands containing carbon (e.g. C≡O) or phosphorus [e.g. P(C$_6$H$_5$)$_3$] could be easily observed directly in terms of the NMR chemical shift.[3] Metal–ligand NMR coupling constants between the NMR active nuclei in the ligand (e.g. ^{31}P) and an NMR active nucleus of the central metal atom (e.g. ^{183}W) have also been widely employed to study metal–ligand interactions, especially for phosphorus donor ligands.[4] Metal–phosphorus bond properties are of great fundamental importance due to the widespread use of phosphorus-containing ligands in metal complexes used in various catalytic processes.[5]

The development of routine metal NMR spectroscopy has recently provided a direct probe of the metal environment[6] and enables one to observe metal–phosphorus coupling constants of metal nuclei which are difficult to observe via ^{31}P NMR spectroscopy (e.g. ^{95}Mo).[7] Studies in our laboratory over the past few years have centred on probing the effects of a number of ligand systems on the molybdenum metal centre in diamagnetic molybdenum metal complexes via ^{95}Mo NMR spectroscopy. ^{95}Mo NMR spectroscopy is well established as a sensitive probe of the molybdenum metal atom in several oxidation states.[8] Our studies on molybdenum(0) carbonyl complexes have shown the chemical shift range for Mo(CO)$_5$L (L = P, As, Sb or N donating ligand) to exceed 400 ppm[9] and to exceed 800 ppm for Mo(CO)$_4$L$_2$ complexes.[10] Our recent study on Mo(CO)$_5$L complexes (L = substituted pyridine ligands) have shown a direct correlation between the σ-bonding ability, as portrayed by the pK_a of the pyridine ligands, and the ^{95}Mo NMR chemical shift [$\delta(^{95}\text{Mo})$] over a range of almost 70 ppm.[11] In contrast, $\delta(^{95}\text{Mo})$ values were surprisingly similar for some [Mo(CO)$_5$(*p*-X-C$_6$H$_4$)$_3$P] complexes involving phosphines of varying basicity.[9] To investigate these effects further we have chosen the system Mo(CO)$_3$(bipy)L (where bipy = 2,2′-bipyridine and L = various phosphine donor ligands). By systematically changing L, we hoped to probe the nature of the bonding between a d^6 metal centre in a low valent oxidation state, and carbon monoxide, a bidentate α-diimine ligand and various phos-

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phorus donor ligands. The reasons for choosing this system involve the fundamental importance of CO, α-diimine and phosphine ligands to coordination, catalytic and electrochemical chemical processes.[12,13] The ability of several commonly accepted parameters (e.g. cone angle (Θ), χ electronic parameter, pK_a, Kabachnik's $\Sigma\sigma^{\phi}$ values, etc.) in quantitatively describing the nature of metal–phosphorus bonding was also the subject of critical scrutiny[14] during this investigation.

EXPERIMENTAL

All reactions and manipulations were carried out under a dry oxygen-free dinitrogen atmosphere. The solvents used were all reagent grade. $Mo(CO)_6$, PMe_3, 2,2′-bipyridine, PBu_3 and trimethylamine oxide dihydrate (TMNO) were purchased from Aldrich Chemical Co. PPh_3 was purchased from Pressure Chemical Co. Tetrabutylammonium iodide (Bu_4NI) was purchased from Fisher Scientific Co. $P(p\text{-}Me\text{-}C_6H_4)_3$, $P(p\text{-}N(CH_3)_2\text{-}C_6H_4)_3$, $P(p\text{-}F\text{-}C_6H_4)_3$ and $P(p\text{-}Cl\text{-}C_6H_4)_3$ were acquired from Strem Chemical Co. and $P(p\text{-}OCH_3\text{-}C_6H_4)_3$ was bought from Columbia Organic Co. Inc. All were used without further purification. NMR measurements were performed in septum-capped 10 mm NMR tubes on freshly prepared samples at room temperature (23 ± 2°C). ^{31}P NMR spectra were recorded in CH_3CN solutions on a Bruker WH-400 spectrometer operating at 161.92 MHz. Chemical shifts are reported as positive to high frequency of external 85% phosphoric acid. ^{95}Mo NMR spectra were recorded on the same instrument or on a Bruker CXP-200 NMR spectrometer, operating at 26.08 or 13.04 MHz, respectively, from naturally abundant ^{95}Mo using saturated CH_3CN solutions. Chemical shifts are relative to external aqueous 2 M K_2MoO_4 at pH 11. Duplicate ^{95}Mo results were obtained at both operating fields, so field effects are termed to be negligible for this series. IR spectra were recorded on a Nicolet 20 DXC FT–IR spectrometer from CH_2Cl_2 solutions in 0.5 mm NaCl solution cells and are accurate to ± 0.5 cm^{-1}. $Mo(CO)_4$bipy was prepared by a published method.[15] In a typical synthesis, 0.3 g of $Mo(CO)_4$ bipy in 20 cm^3 CH_3CN was heated to reflux for 15 min with an equimolar quantity of TMNO[16] or a catalytic amount of Bu_4NI and an equimolar quantity of the desired phosphine ligand. As the PPh_3 derivative of this series is known,[17] the species studied were not isolated but observed entirely *in situ* using at least duplicate repetitions. Note that although the reactions were carried out in CH_3CN, at no time was $[Mo(CO)_3(bipy)(CH_3CN)]$ observed by IR spectroscopy, so it is assumed to be a short-lived intermediate in the decarbonylation–phosphine addition process.[18] The complexes synthesized are all the thermodynamically stable facial isomers as indicated by their IR spectra.[2]

RESULTS AND DISCUSSION

The ^{31}P NMR and reference data for the free phosphines and complexes appear in Table 1. For the complexes, the carbonyl stretching frequencies and the ^{95}Mo NMR data appear in Table 2. Several trends can be seen. First, the value of the CO stretching frequency representative of the A_1 mode does not greatly change throughout the series. In fact, any electronic differences between $P(p\text{-}Me\text{-}C_6H_4)_3$ and $P(p\text{-}OCH_3\text{-}C_6H_4)_3$ are not resolved by the A_1 mode. The sum of all CO stretching vibrations [$\Sigma\sigma(CO)$] may, in fact, be a better reflection of the net effect on the CO ligands of varying the phosphine.

Relationships between the measured values for $\nu(C{\equiv}O)$, $\Delta\delta(^{31}P)$ and $\delta(^{95}Mo)$ run from good to excellent within the series. The $\Delta\delta(^{31}P)$ values relate to the $\delta(^{95}Mo)$ values (correlation coefficient $r = 0.902$) and to the changes in the $\Sigma\nu(C{\equiv}O)$ values ($r = 0.992$). In turn, the $\Sigma\nu(C{\equiv}O)$ values relate well to the $\delta(^{95}Mo)$ values ($r = 0.962$). This trend is expected when the steric bulk of the phosphorus ligand remains constant,[21] as is the case here.

The $\Delta\delta(^{31}P)$ chemical shift values show a general decrease with increasing ligand substituent electron-donating ability, indicating less net electron donation by the phosphine with increasing ligand Brönsted basicity. This trend has also been observed for other molybdenum(0) carbonyl complexes.[22(a)] Electron density around the molybdenum atom, as indicated by $\delta(^{95}Mo)$, is not greatly affected by the changes in the electronic

Table 1. Data for $P(X\text{-}C_6H_4)_3$ phosphines and *fac*-$[Mo(CO)_3(bipy)\{P(p\text{-}C_6H_4\text{-}X)_3\}]$ complexes

X	$\delta(^{31}P)$ (ppm)[a]	pK_a[a]	$\Sigma\sigma^{\phi b}$	$\delta(^{31}P)$ (ppm)[c]	$\Delta(\delta^{31}P)$[d]
Cl	−8.7	1.03	−0.87	37.0	45.7
F	−9.3	1.97	−0.96	35.9	45.2
H	−6.3	2.73	−1.77	37.5	43.8
CH_3	−8.3	3.84	−2.16	35.2	43.5
OCH_3	−10.6	4.59	−2.22	33.1	43.5
$N(CH_3)_2$	−11.7	8.65	−3.51	30.3	42.0

[a] Free ligand values, ref. 19.
[b] Reference 20.
[c] Complex values, in CH_3CN solution.
[d] $\Delta(\delta^{31}P) = \delta(^{31}P)_{complex} - \delta(^{31}P)_{free\ ligand}$.

Table 2. IR spectral data of carbonyl region and ^{95}Mo NMR data of [$Mo(CO)_3(bipy)\{P(p\text{-}C_6H_4\text{-}X)_3\}$] complexes

X	$\nu(C{\equiv}O)$ (cm^{-1})^a	$\Sigma[\nu(CO)]$	$\delta(^{95}Mo)$ (ppm)^b	J_{Mo-P} (Hz)	$\Delta\nu_{1/2}$ (Hz)
Cl	1920, 1825, 1792	5537	−1061.1	127	51
F	1918, 1826, 1791	5535	−1060.0	132	30
H	1915, 1816, 1791, 1913, 1820, 1792,^{c} 1919, 1822, 1789^d	5522	−1062.8	127	18
CH_3	1913, 1815, 1788	5516	−1063.8	128	32
OCH_3	1913, 1814, 1787	5514	−1063.0	127	61
$N(CH_3)_2$	1908, 1806, 1783	5497	−1065.5	129	43

[a] In CH_2Cl_2 solution.

[b] In CH_3CN solution.

[c] Reference 17(a), in $C_2H_4Cl_2$ solution.

[d] Reference 17(b), in $CHCl_3$ solution.

properties of the phosphine since the $\delta(^{95}Mo)$ values span a range of only about 6 ppm. This slight shift is not adequately explained by plotting $\delta(^{95}Mo)$ vs the phosphine ligand pK_a (Table 1) (correlation coefficient (r) is only 0.880) nor by the Tolman χ_i value ($r = 0.908$).[13] This lends support to two conceptual ideas, one of which we discuss here, while the other has been discussed previously.[23] Firstly, the lack of good correlation with Tolman's χ_i values lends support to our idea that $\Sigma\nu(CO)$ is a better reflection of the effect of the nature of PR_3 then the A_1 stretching mode is alone, since χ_i values are based solely on the A_1 stretching mode of various $Ni(CO)_3L$ (L = phosphorus ligands) complexes.[13] Secondly, the lack of correlation with the measured value of the ligand's pK_a supports the argument that pK_a values are not an appropriate measure of the interaction between phosphines and soft acid species such as low-valent transition metal centres.[23] The justification here lies in the fact that pK_a values are dependent on the interaction between the phosphine and the hard acid, H^+. An acceptable correlation ($r = 0.957$) is found between $\delta(^{95}Mo)$ and the Kabachnik $\Sigma\sigma^{\phi}$ parameter (Fig. 1), indicating that $\Sigma\sigma^{\phi}$ may be the better experimental parameter for this type of series. The Kabachnik substituent parameters,[20] derived from ionization data of phosphorus acids using a Hammett-type relationship, have been noted by other workers[13,19] to be good measures of electronic effects for phosphines. The Mo—P coupling constants are basically uniform throughout the series indicating that molybdenum–phosphorus σ-bonding character is essentially the same throughout the series. Since the phosphines must be donating different amounts of electron density in total, as measured by $\Delta(\delta^{31}P)$, the other ligands present in the system must be serving in some way to compensate for the difference. A plot of $\Sigma\sigma^{\phi}$ vs $\Sigma\nu(CO)$ yields an excellent correlation ($r = 0.998$) (Fig. 2), indicating that the electronic differences of the phosphines are adequately measured by summing the CO stretching frequency vibrations. This trend has been observed previously for a series of $Mo(CO)_5$(py-R)

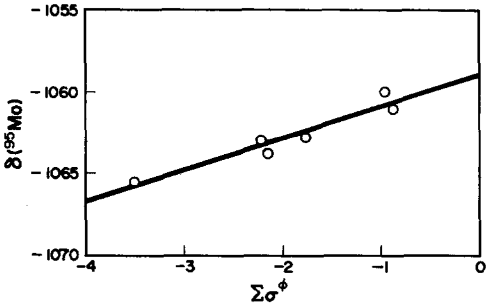

Fig. 1. Plot of $\delta(^{95}Mo)$ vs $\Sigma\sigma^{\phi}$ for [$Mo(CO)_3$(bipy) $\{P(X\text{-}C_6H_4)_3\}$] complexes.

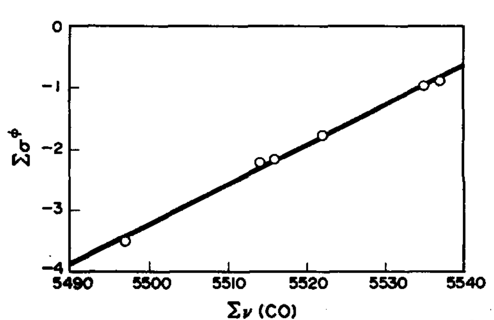

Fig. 2. Plot of $\Sigma\sigma^{\phi}$ vs $\Sigma\nu(CO)$ for [$Mo(CO)_3$(bipy) $\{P(X\text{-}C_6H_4)_3\}$] complexes.

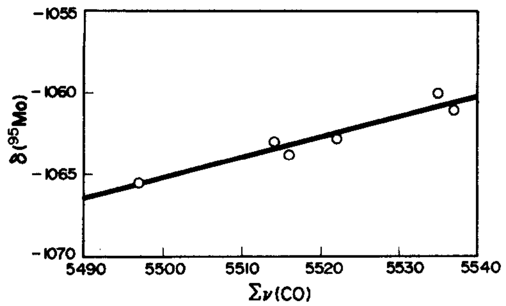

Fig. 3. Plot of $\delta(^{95}Mo)$ vs $\Sigma\nu(CO)$ for $[Mo(CO)_3(bipy)\{P(X\text{-}C_6H_4)_3\}]$ complexes.

(py-R = substituted pyridine ligand) complexes.[24] The $\delta(^{95}Mo)$ value is directly affected by the different electronic nature of $P(p\text{-}X\text{-}C_6H_4)_3$ and this trend is also reflected by the net change on the CO ligands (Fig. 3), but phosphorus σ-donor character is not significantly changed. This result tends to indicate that the CO ligands are responsible for compensating for the lesser or greater donating ability of $P(p\text{-}X\text{-}C_6H_4)_3$ compared to PPh_3. The effect of the bidentate α-diimine ligand, 2,2′-bipyridine, is likely uniform within this series since $\Sigma\sigma^{\phi}$ relates directly to $\Sigma\nu(CO)$. The general compensation of overall metal electron density by CO regardless of X in $P(p\text{-}X\text{-}C_6H_4)_3$ has the possibility of steric hindrance as its basis. The bulkiness of PPh_3 ($\Theta = 145°$),[13] compared to many other phosphine ligands, may not allow the phosphine to get close enough to the molybdenum centre for its full electronic character to greatly influence the metal's electron sphere. To test if this was indeed the case, we synthesized two other complexes $[Mo(CO)_3(bipy)(PMe_3)]$ and $[Mo(CO)_3(bipy)(PBu_3)]$, where the ligand PR_3 had a smaller steric size than PPh_3 but electronic capabilities, measured by $\Sigma\sigma^{\phi}$, within the same range.

The PBu_3 complex [$\nu(CO)$: 1908, 1806, 1784 cm^{-1}; $\delta(^{31}P)$: $+3.70$, $\Delta\delta(^{31}P) = 34.0$ ppm; $\delta(^{95}Mo) = -1071.2$ ppm, $^{1}J_{MoP} = 125$ Hz] produces a more pronounced effect on the molybdenum centre, shielding it by a further 5.7 ppm over the $P(p\text{-}NMe_2\text{-}C_6H_4)_3$ complex. PBu_3 is producing virtually the same net electronic effect on the CO ligands ($\Sigma\nu(CO) = 5498$) as compared to $P(p\text{-}NMe_2\text{-}C_6H_4)_3$ ($\Sigma\nu(CO) = 5497$) which is not unexpected since the $\Sigma\sigma^{\phi}$ values for these two ligands, -3.66 and -3.51,[20] respectively, are very similar. The further effects of PBu_3 over the PPh_3 derivatives in shielding the metal centre may therefore be a result of the smaller steric size of PBu_3 ($\Theta = 132°$) over PPh_3. This allows PBu_3 to move closer to the metal centre and hence produce stronger overall molybdenum shielding. This is also seen with the PMe_3 complex [$\nu(CO)$: 1910, 1810, 1785 cm^{-1}; $\delta(^{31}P)$: -15.2, $\Delta\delta^{31}P = 45.8$ ppm; $\delta(^{95}Mo) = -1076.8$ ppm, $^{1}J_{MoP} = 130$ Hz]. The poorer electron donor PMe_3 ($\Sigma\sigma^{\phi} = -2.88$ vs -3.66 for PBu_3), still puts considerably more electron density on the metal centre than does PPh_3 [$\delta(^{95}Mo) = -1062.8$ ppm, $\Sigma\sigma^{\phi} = -1.77$].

Thus, the CO ligands appear to restabilize net metal electron density only to some maximum extent, dictated not only by phosphine electronic but by steric properties. Only when the phosphine is small enough to get close to the metal centre can its electronic capabilities be seen to truly influence net metal electron density to a significant extent. This "push–pull" mechanism between phosphine σ-donor ability and steric ligand bulk is of great fundamental importance since it will greatly influence the design of metal catalytic molecules. The relative importance of steric vs electronic effects on molybdenum(0) carbonyl complexes has also been demonstrated in several earlier NMR studies by Gray and others.[21,22]

An interesting anomaly in this series is the fact that $P(p\text{-}OCH_3\text{-}C_6H_4)_3$ shields the molybdenum nucleus to a lesser extent than $P(p\text{-}CH_3\text{-}C_6H_4)_3$. This observation is also seen for the $Mo(CO)_5PR_3$ complexes,[9] although the shielding difference in that case is a more pronounced one. The reason for this is currently unclear, since steric effects in both cases are obviously uniform. It does indicate, however, that various groups may be less able to affect the metal nucleus than their $\Sigma\sigma^{\phi}$ (or pK_a) values would indicate. This dictates caution in describing metal electron density based solely on measured parameters of the free ligands only.

Our attempts to correlate relative shielding of the molybdenum metal nucleus to the Mo—P bond length have proved ineffective. The Mo—P bond lengths for $Mo(CO)_5PPh_3$ and $[Mo(CO)_5P(p\text{-}CH_3\text{-}C_6H_4)_3]$ are virtually identical, being 2.560 and 2.562 Å, respectively,[25,26] but $\delta(^{95}Mo)$ values differ by 7 ppm,[9] similar to the difference between $[Mo(CO)_3(bipy)\{P(p\text{-}CH_3O\text{-}C_6H_4)_3\}]$ and $[Mo(CO)_3(bipy)(PBu_3)]$. This similarity of bond lengths was noted in the recent related study of several iron(II) phosphine complexes where bond lengths and σ-donor/π-acceptor ability of the phosphine ligands do not appear to correlate.[14(a)]

Our results also show one other important factor. Giering and co-workers state in their discussion of the relative bonding ability of phosphine ligands that: "Undoubtedly, the terminal carbonyl stretching frequencies {of their $[(\eta^5\text{-}C_5H_5)Fe(CO)(COCH_3)(PR_3)]$ complexes} are directly dependent on the electron density of the metal to which the CO is bonded".[14(a)] However, we have clearly shown, by comparing the $\delta(^{95}Mo)$ values of [$Mo(CO)_3(bipy)(PBu_3)$] and [$Mo(CO)_3(bipy)\{P(p\text{-}NMe_2\text{-}C_6H_4)_3\}$], both of which have virtually identical CO stretching frequencies, that their statement is not universally valid. Thus, the best probe of metal electron density is not by observation of the surrounding ligands but by observing the metal centre itself.

Related ^{95}Mo NMR studies currently underway in our laboratory are centred around further probing the nature of the effects of phosphines and phosphites on molybdenum environments.

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REFERENCES

1. L. E. Orgel, *Inorg. Chem.* 1962, **1**, 25.
2. C. Kraihanzel and F. A. Cotton, *J. Am. Chem. Soc.* 1962, **84**, 4432.
3. For example: (a) G. M. Bodner, *Inorg. Chem.* 1975, **14**, 2694; (b) R. Mathieu, M. Lenzi and R. Poilblanc, *Inorg. Chem.* 1970, **9**, 2030; (c) S. O. Grim, R. M. Singer, A. W. Johnson and F. J. Randall, *Coord. Chem.* 1978, **8**, 121.
4. (a) S. O. Grim, D. A. Wheatland and W. McFarlane, *J. Am. Chem. Soc.* 1967, **89**, 5573; (b) G. G. Mather, A. Pidcock and G. J. N. Rapsey, *J. Chem. Soc., Dalton Trans.* 1973, 2095.
5. For example: (a) W. W. Porterfield, *Inorganic Chemistry*, Ch. 13. Addison-Wesley, Don Mills, Ontario (1984); (b) E. C. Alyea and D. W. Meek (Eds), *Catalytic Aspects of Metal Phosphine Complexes*. Advances in Chemistry Series **196**, American Chemical Society, Washington, D.C. (1982); (c) L. H. Pignolet (Ed.), *Homogeneous Catalysis with Metal Phosphine Complexes*. Plenum Press, New York (1983).
6. (a) J. J. Dechter, *Prog. Inorg. Chem.* 1985, **33**, 393; (b) J. B. Lambert and F. G. Riddell (Eds), *The Multinuclear Approach to NMR Spectroscopy*. Reidel Publishing Company, Dordrecht (1983); (c) J. Mason, *Chem. Rev.* 1987, **87**, 1299.
7. A. F. Masters, G. E. Bossard, T. A. George, R. T. C. Brownlee, M. J. O'Connor and A. G. Wedd, *Inorg. Chem.* 1983, **22**, 908.
8. M. Minelli, J. H. Enemark, R. T. C. Brownlee, M. J. O'Connor and A. G. Wedd, *Coord. Chem. Rev.* 1985, **68**, 169.
9. E. C. Alyea and A. Somogyvari, *Transition Met. Chem.* 1987, **12**, 310.
10. E. C. Alyea and A. Somogyvari, *Can. J. Chem.* 1988, **66**, 397.
11. E. C. Alyea, K. J. Fisher and R. A. Gossage, *Spectrochim. Acta* 1989, **45A**, 203.
12. M. S. Wrighton (Ed.), *Inorganic and Organometallic Photochemistry*. Advances in Chemistry Series **168**, American Chemical Society, Washington, D.C. (1978).
13. C. A. Tolman, *Chem. Rev.* 1977, **77**, 313 and refs therein.
14. (a) M. M. Rahman, H. Y. Liu, K. Eriks, A. Prock and W. P. Giering, *Organometallics* 1989, **8**, 1; (b) M. M. Rahman, H. Y. Liu, A. Prock and W. P. Giering, *Organometallics* 1987, **6**, 650; (c) M. N. Golovin, M. M. Rahman, J. E. Belmonte and W. P. Giering, *Organometallics* 1985, **4**, 1981.
15. E. W. Abel, G. Bennett and G. Wilkinson, *J. Chem. Soc.* 1959, 2323.
16. T. S. A. Hor, *Inorg. Chim. Acta* 1988, **149**, 169.
17. (a) M. H. B. Stiddard, *J. Chem. Soc.* 1963, 756; (b) L. W. Houk and G. R. Dobson, *J. Chem. Soc. A* 1966, 317.
18. L. W. Houk and G. R. Dobson, *Inorg. Chem.* 1966, **5**, 2119.
19. T. Allman and R. Goel, *Can. J. Chem.* 1982, **60**, 716.
20. T. A. Mastryukova and M. I. Kabachnik, *Russ. Chem. Rev.* 1969, **38**, 795.
21. (a) G. M. Gray, *Inorg. Chim. Acta* 1984, **81**, 157; (b) G. M. Gray, R. J. Gray and D. C. Berndt, *J. Mag. Reson.* 1984, **57**, 347.
22. (a) G. M. Gray and R. J. Gray, *Organometallics* 1983, **2**, 1026; (b) G. M. Gray and C. S. Kraihanzel, *Inorg. Chem.* 1983, **22**, 2959; (c) A. M. Bond, S. W. Carr and R. Colton, *Organometallics* 1984, **3**, 541.
23. W. H. Thompson and C. T. Sears Jr, *Inorg. Chem.* 1977, **16**, 769.
24. H. O. Desseyn, B. J. van der Veken, J. R. Moss, B. J. Smith, P. Verhoeven and D. A. Thornton, *Spectrochim. Acta* 1984, **40A**, 467.
25. F. A. Cotton, D. J. Darensbourg and W. H. Ilsley, *Inorg. Chem.* 1981, **20**, 578.
26. E. C. Alyea, G. Ferguson and A. Somogyvari, *Organometallics* 1983, **2**, 668.