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^{95}Mo studies of ligands relevant to dinitrogen fixation: NMR spectrochemical series based on ^{95}Mo shielding *

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Abstract

^{95}Mo NMR shifts and coupling constants are related to the ligand properties and stereochemistry of a range of phosphine complexes containing N_2 or other *N*-ligating groups. With comparable co-ligands, the ^{95}Mo shielding decreases in the sequence $H^- > CO > PR_3 > PAr_3 > N_2 > N_3^- \geqslant NCAr > NO^+ > N{=}NR^+ > {=}N{-}NR_2^{2-} >$ *O*-ligands, depending on the balance of ligand field strength and nephelauxetic effects. The shielding decreases with increase in Mo–N bond order from Mo–N_2 to Mo–NNR and to Mo=NNR_2. *Trans* influences on $^1J(^{95}Mo^{31}P)$ coupling constants are similar for N_2 and the phosphines.

Introduction

Molybdenum complexes containing the dinitrogen ligand are important as model compounds in the study of dinitrogen fixation by the molybdoenzyme nitrogenase, since they are made from molecular N_2 and allow the dinitrogen to be reduced to ammonia under mild conditions [1]. Useful information on ligand properties in metal complexes may be gained from NMR spectroscopy of the metal nucleus, because of its inherent sensitivity to the coordination environment [2]: for ^{95}Mo, the chemical shifts in metal complexes cover a range of over 7000 ppm, depending on the ligation [3–5]. To date the nuclear electric quadrupole of ^{95}Mo has impeded attempts to study molybdoenzymes by ^{95}Mo NMR spectroscopy because of the line-broadening in large molecules, but the ^{95}Mo quadrupole moment is relatively

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* We have pleasure in dedicating this paper to Professor Colin Eaborn, for his distinguished contributions to organometallic chemistry.

small, so that resonances and even some spin–spin couplings may be resolved in smaller molecules, with faster tumbling in solution.

Dinitrogen is bound as a ligand in complexes with $\{MoP_5\}$, $\{MoP_4\}$, and $\{MoP_3\}$ cores, where P is the ligating phosphorus of a mono- or di-tertiary phosphine. Alkylphosphine (compared with arylphosphine) co-ligands confer greater solubility, so that ^{95}Mo spectra may often be obtained at frequencies as low as 5.80 MHz, and PMe_3 complexes [6] in particular give quite narrow lines.

Although higher sensitivity (obtainable at higher field) is required for the arylphosphine complexes, these tend to be more stable and offer further scope for the study of substituents which demonstrate electronic and steric effects of the ligands. In *trans*-$[Mo(N_2)_2(diphos)_2]$ * complexes, the lability of the dinitrogen ligands allows further comparisons within the *trans*-$[Mo(N_2)(L)(diphos)_2]$ and $[Mo(L)(L')(diphos)_2]$ series, particularly with other nitrogen-ligating groups such as nitrile, amine, azide, or nitrosyl, and other ligands relevant to dinitrogen fixation processes, such as diazenide and hydrazide(2 −). Some of our preliminary work has been reported [7].

Of particular interest is the comparison of ^{95}Mo results for N_2 and related ligands with the results obtained in ^{51}V resonance by Rehder and coworkers [8], since forms of nitrogenase have now been found which contain vanadium and not molybdenum [9].

Results and discussion

^{95}Mo linewidths

Tables 1 and 2 show the ^{95}Mo NMR spectroscopic results. The low-viscosity solvents minimise quadrupolar relaxation rates, and linewidths of 15–20 Hz were observed for the small PMe_3 complexes in thf. Unexpectedly, the sharpest lines (with $W_{1/2}$ 10 Hz) were observed for *mer*-$[Mo(N_2)_3(PPr^n_2Ph)_3]$. The larger size of these phosphines is perhaps balanced by the smaller number of them; but $[ML_3L'_3]$ complexes usually give broader lines for meridional than for facial stereochemistry because of the higher local symmetry (lower electric field gradient) at the metal in the facial configuration [10]. Linewidths of 10 and 200 Hz were reported for *fac* and *mer* isomers of $[Mo(CO)_3\{P(OPh)_3\}_3]$, respectively [11]. Meridional stereochemistry was, however, demonstrated for *mer*-$[Mo(N_2)_3(PPr_2Ph)_3]$ in the solid state by X-ray crystallography [12], and confirmed for the solution phase by ^{31}P [12] and ^{15}N [13] NMR spectroscopy.

Broader lines were observed for the bulkier arylphosphine co-ligands, up to 200 Hz in width for the bulkiest. The lines may be sharpened by measurement at higher temperatures, but this was avoided because of the lability of many of the complexes (examples of which are given below). Linewidths are not given for the $[Mo(L)_2(dppe)_2]$ compounds in Tables 1 and 2 for which the ^{95}Mo^{31}P coupling was not resolved, often because of low sensitivity.

^{95}Mo shielding

As shown in Table 1, the variations in coordination sphere in the dinitrogen complexes give a range of nearly 800 ppm in ^{95}Mo shifts, and these can be related to

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* Ligand abbreviations are defined in Table 1, footnote *a*.

Table 1

^{95}Mo NMR spectroscopic parameters in dinitrogen phosphine complexes and related compounds

Complex [a]	$\delta(^{95}\mathrm{Mo})$ [b] (ppm)	$W_{1/2}$ [c] (Hz)	$\lvert ^1J(^{95}\mathrm{Mo}^{31}\mathrm{P})\rvert$ [d] (Hz)	ν_0 (MHz)
$[\mathrm{Mo(CO)_6}]$	−1855		–	
cis-$[\mathrm{Mo(CO)_4(dppe)}]$ [e]	−1775	50	134	5.80
cis-$[\mathrm{Mo(CO)_2(dppe)_2}]$	−1486		n.r.	23.47
trans-$[\mathrm{Mo(CO)_2(dppe)_2}]$	−1451		n.r.	23.47
trans-$[\mathrm{Mo(N_2)(CO)(dppe)_2}]$ (toluene)	−1167			26.08
trans-$[\mathrm{Mo(N_2)_2(depe)_2}]$ [f]	−1022	65	185	5.80
trans-$[\mathrm{Mo(N_2)_2(depe)(dppe)}]$ [f]	−899	65	185	5.80
trans-$[\mathrm{Mo(N_2)_2(dptpe)_2}]$ [f]	−793	50	175	26.08
	−776 [g]	85	205	13.0
trans-$[\mathrm{Mo(N_2)_2(dppe)_2}]$ [f]	−787	50	180	26.08
$[\mathrm{Mo(^{15}N_2)(PMe_3)_5}]$	−178 [h]	15	170	23.47
trans-$[\mathrm{Mo(N_2)_2(PMe_2Ph)_2(dppe)}]$	−701	20	175	23.47
trans-$[\mathrm{Mo(N_2)(NCC_6H_4OMe\text{-}4)(dppe)_2}]$	−667	170	170	26.08
cis-$[\mathrm{Mo(N_2)_2(PMe_3)_4}]$	−637	20	175	5.80
trans-$[\mathrm{Mo(N_2)_2(PMePh_2)_4}]$ [f]	−464	25	190	5.80
cis-$[\mathrm{Mo(N_2)_2(PMePh_2)_4}]$	−455	25	n.r.	23.47
mer-$[\mathrm{Mo(N_2)_3(PPr^n{}_2Ph)_3}]$	−392	10	180	23.47

[a] dppe = bis(diphenylphosphino)ethane, depe = bis(diethylphosphino)ethane, dptpe = bis(di-4-tolylphosphino)ethane. [b] Measured at 298 K in solution in thf, unless another solvent is given. Shifts (±1 ppm for the narrower lines) are given relative to 2 *M* aqueous $\mathrm{Na_2[MoO_4]}$ at pH 11, measured at the frequency specified. [c] ±5 Hz, not optimised. [d] ±10 Hz for equivalent phosphines; n.r. = not resolved. For non-equivalent phosphines, different ^1J values were not resolved. [e] Measured at 313 K, Ref. 11. [f] Ref. 7. [g] Measured at 328 K Ref. 21. [h] $\lvert ^1J(^{95}\mathrm{Mo}^{15}\mathrm{N})\rvert$ 32 Hz.

steric and electronic effects. As to steric effects, the replacement of two *cis* monophosphines by a comparable bidentate diphosphine (e.g. $2\mathrm{PR_3}$ by depe, where R is an alkyl group, or $2\mathrm{PRPh_2}$ by dppe) normally increases the transition metal

Table 2

Comparison of ^{95}Mo NMR parameters in dinitrogen, nitrosyl, diazenido and hydrazido(2−) complexes with the *trans*-{Mo(dppe)$_2$} core

Complex [a]	$\delta(^{95}\mathrm{Mo})$ (ppm)
trans-$[\mathrm{MoH_4(dppe)_2}]$(benzene/toluene) [b]	−1865
trans-$[\mathrm{Mo(CO)_2(dppe)_2}]$	−1451
trans-$[\mathrm{Mo(CO)(N_2)(dppe)_2}]$(toluene)	−1167
trans-$[\mathrm{Mo(CO)(NCC_6H_4X\text{-}4)(dppe)_2}]$ X = OMe	−1126
X = H	−1118
X = C(O)Me	−1089
trans-$[\mathrm{Mo(N_2)_2(dppe)_2}]$ [c]	−787
trans-$[\mathrm{Mo(N_2)(NCC_6H_4OMe\text{-}4))(dppe)_2}]$(thf)	−667
trans-$[\mathrm{Mo(N_3)(NO)(dppe)_2}]$ [c]	−614
trans-$[\mathrm{Mo(NCMe)(NO)(dppe)_2}][\mathrm{BF_4}]$ [c]	−553
trans-$[\mathrm{MoBr(NO)(dppe)_2}]$ [c]	−514
trans-$[\mathrm{Mo(N_3)(NNEt)(dppe)_2}]$	−180
trans-$[\mathrm{Mo(NCMe)(NNEt)(dppe)_2}][\mathrm{BPh_4}]$	−140
trans-$[\mathrm{Mo(N_3)(NNHEt)(dppe)_2}]$Br	140

[a] Measured at 26.08 MHz in $\mathrm{CH_2Cl_2}$ solution (unless another solvent is given) at 298 K. [b] Ref. 24. [c] Ref. 7.

shielding when the chelate ring is five-membered (as in the depe, dppe, or other diaryldiphosphinoethane, dArpe, ligands), whether in ^{95}Mo resonance [11], or that of other metals [5,14]. These chelate effects may be related to angular distortion in the coordination sphere. Thus the formation of four-membered rings usually decreases the metal shielding, as does the presence of bulkier substituents in ligands such as phosphines of a particular type [14].

Angular distortion affects two of the three terms that are important in nuclear magnetic shielding, the ligand field splitting and the imbalance of charge in the valence shell of the metal [2]. In the ligand field formulation of Griffith and Orgel [15] for d^6 octahedral complexes, deshielding (δ) is mediated by $d\pi \rightarrow d\sigma^2$ circulations of "non-bonding" electrons in the magnetic field, and increases as the product $\langle r^{-3}\rangle_d \langle 0 | L^2 | 0\rangle \Delta_0{}^{-1}$ (summed over the *d–d* excitations), where r_d is the valence *d* electron radius, $\langle 0 | L^2 | 0\rangle$ the angular momentum term, increasing with the *d* orbital imbalance, and Δ_0 the ligand field splitting. Thus high shielding is associated with ligands high in the spectrochemical series (strong ligands, Δ_0 large) and with larger nephelauxetic effect ($\langle r^{-3}\rangle_d$ small) [2].

Electronic factors are evident in comparisons of the compounds with similar stereochemistry. Compounds with the *trans*-[Mo(N_2)$_2$(dppe)$_2$] core show an approximately additive increase in ^{95}Mo shielding, by about 125 ppm each time, on replacement of the arylphosphine (dppe) with the alkylphosphine (depe). The increase in shielding is attributable to the greater nephelauxetic effect of the alkylphosphine, which is the more basic (tending to reduce the radial term $\langle r^{-3}\rangle$); and also to its greater ligand field strength. The metal shielding increases also on replacement of $PMePh_2$ by PMe_2Ph or PMe_3, except that it is lower in *cis*-[Mo(N_2)$_2$(PMe_2Ph)$_4$] than in *trans*-[Mo(N_2)$_2$($PMePh_2$)$_4$]. For similar ligands, however, lower shielding is normally observed for the *cis* than the *trans* geometry; on a point charge model, the electric field gradient at the metal nucleus is smaller for *cis* than *trans* geometry of given ligands [10], but ligand field splittings may be smaller for *cis* than *trans*.

In the *trans*-[Mo(N_2)$_2$(dArpe)$_2$] series (where Ar = C_6H_4Z-4, with Z = MeO, Me (i.e. dptpe), H (i.e. dppe), Cl, or CF_3) the ^{95}Mo shielding decreases with decrease in electron donor ability of the 4-substituent in the aryl group [7], as shown by increase in the Hammett σ_p value [16]. The correlation coefficient of $\delta(^{95}\text{Mo})$ with σ_p is 0.982. There is a corresponding correlation of the oxidation potential $E_{1/2}^{ox}$ of these compounds with σ_p, with correlation coefficient 0.995 [17]. Oxidation is facilitated by increased charge at the metal, with decrease in σ_p. These compounds also show some parallelism of the ^{95}Mo and the ^{31}P shifts, but the phosphorus shifts are the more sensitive to steric effects of the Z-substituents. Less good correlations are observed of $\delta(^{95}\text{Mo})$ or $E_{1/2}^{ox}$ with the Hammett $\sigma_p{}^+$ parameter in the *trans*-[Mo(N_2)$_2$(dArpe)$_2$] series, indicating that the trends in $\delta(^{95}\text{Mo})$ and oxidation potential are determined primarily by changes in inductive effects of the phosphine ligands. Decrease in $\sigma_p{}^+$ does, however, correlate with decrease in the N_2 stretching frequency (coefficient 0.999), reflecting increased back-bonding from the metal to N_2 with increase in charge donation from the phosphines [17].

In the dinitrogen complexes without chelating phosphines, ^{95}Mo is progressively

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* Ligand abbreviations are defined in Table 1, footnote a.

deshielded with increasing substitution of phosphine by the dinitrogen ligand: the greatest deshielding is observed in the tris(dinitrogen) compound, with $\delta(^{95}\mathrm{Mo})$ -392 ppm, despite the presence of the relatively strong PR_2Ph ligands. These phosphines are sufficiently bulky that they push the dinitrogen groups together and lengthen the Mo–N bonds in the *trans*-N_2 ligands in the solid state [12], so the distortion no doubt contributes to the deshielding.

Table 2 compares ^{95}Mo shifts in complexes with the *trans*-$\{\mathrm{Mo(dppe)_2}\}$ core, and axial dinitrogen or other nitrogen-ligating groups relevant to dinitrogen fixation processes. With successive protonations of Mo–N_2 under mild conditions, diazenido (Mo–N=NH) and hydrazido(2 –) (Mo=N–NH_2) ligands can be isolated on the pathway to ammonia [1], while NO poisons nitrogenase. The nitrosyl, diazenido and hydrazido(2 –) ligands are linear in the compounds in Table 2, and so are considered as NO^+, $(N{=}NH)^+$, and $(=NNR_2)^{2-}$, respectively. All the complexes, therefore, formally contain $\mathrm{Mo^0}$, except for the hydrazido(2 –) complex and the tetrahydride, formally $\mathrm{Mo^{IV}}$. In shielding comparisons, however, the formal oxidation state may not be important. The charge on the metal in the tetrahydride, for example, is not very different from that in the $\mathrm{Mo^0}$ complexes with strong ligands (CO or phosphine), and the shielding ranges for mononuclear $\mathrm{Mo^0}$, $\mathrm{Mo^{II}}$ and $\mathrm{Mo^{IV}}$ complexes show considerable overlap. The high shielding in the tetrahydride complex parallels the strong increase in ^{95}Mo shielding with protonation in η^5-cyclopentadienylmolybdenum compounds, as from $[\mathrm{Mo(cp)_2H_2}]$ with $\delta(^{95}\mathrm{Mo})$ -2507 ppm to $[\mathrm{Mo(cp)_2H_3}]^+$ with $\delta(^{95}\mathrm{Mo})$ -2953, despite the increase in formal oxidation state from $\mathrm{Mo^{IV}}$ to $\mathrm{Mo^{VI}}$. The shielding increases by 450 ppm as the stabilisation of a $d\pi$ electron pair, by bonding to hydrogen, removes a relatively low energy d–d paramagnetic circulation [3].

The combined evidence from the compounds in Tables 1 and 2 thus gives an NMR spectrochemical series of decrease in metal nucleus shielding as $H^- > CO > PR_3 > PAr_3 > N_2 > N_3^- \geqslant NCAr > NO^+ > N{=}NR^+ > {=}N{-}NR_2^{2-} >$ *O*-ligands. The ^{95}Mo shielding decreases with increase in Mo–N bond order from Mo–N_2 to Mo–NNR and to Mo=NNR_2, cf. the deshielding with increase in metal–metal bond order in molybdenum dimers [3]. In the cations, the decrease in nephelauxetic effect contributes to deshielding. The bulk of the NCAr ligand may account for some of the deshielding relative to the N_2 ligand or to MeCN: ^{15}N NMR studies of *trans*-$[\mathrm{Mo(^{15}N)_2(NCC_6H_4X\text{-}4)(diphos)_2}]$ compounds have shown linear correlations of $\delta(^{15}\mathrm{N})$ and $E_{1/2}^{\mathrm{ox}}$ for the complexes with Hammett σ_p parameters for the X substituent of the benzonitrile, indicating transfer of electronic charge via the metal with increase in $(\sigma + \pi)$ electron-releasing properties of the nitrile [18], confirming the "spectrochemical" influence of the nitrile. A similar trend in $\delta(^{95}\mathrm{Mo})$ is evident for the carbonyl complexes *trans*-$[\mathrm{Mo(CO)(NCC_6H_4X\text{-}4)(dppe)_2}]$ (with $X = H$, OMe, or C(O)Me), as shown in Table 2.

In transition metal NMR spectroscopy, the ligand-dependence of the shielding [2] follows the ordering of the optical spectrochemical series, so long as ligating atoms from the same row of the Periodic Table are being compared. Down the group of the ligand, nephelauxetic effects tend to increase (with increase in ligand polarisability, and covalency), thus increasing the metal shielding. Ligand field splittings, however, tend to decrease down the group, decreasing the shielding, except for the nitrogen group in which phosphines, with better σ-donor, π-acceptor properties, are stronger ligands than groups with ligating nitrogen [2].

For ligators from the same row, the effects of the energy term (Δ_0) and the radial term reinforce, the shielding decreasing as $C > N > O$, etc., as in the series given above. This is observed also in substituted Mo^0 carbonyl derivatives, $[Mo(CO)_5L]$, $[Mo(CO)_4L_2]$, etc., which give a ^{95}Mo shielding series for the L ligands as $CO > PR_3 > PAr_3 > NCMe \simeq$ amines > py > *O*-ligands [4]. A similar series is given by $[V(CO)_5L]^-$ complexes, in which the range of L ligands now includes N_2, and the ^{51}V shielding decreases as $H^- > CO > PPh_3 > N_2 > NCPh >$ amines > py > *O*-ligands [8]. Clearly N_2 belongs with the *N*-ligators, but is a stronger ($\sigma + \pi$) ligand than the others, the lowest shielding being observed for the M=N-bonded hydrazide.

A further comparison of interest is with partial centre shifts in Fe^{II} Mössbauer spectroscopy [19]. These reflect the balance of ($\sigma + \pi$) properties of the ligands, since increase in σ-donor and (or) π-acceptor ability increases *s*-electron density at the nucleus and decreases the centre shift. The ranking correlates (inversely) with the spectrochemical series, and is particularly helpful when ligand field bands are not observable in the optical spectra. Partial centre shift values in Fe^{II} complexes increase as $NO^+ < H^- < CO < PPh_3 <$ py $\sim$ amines $< N_3^- <$ *O*-ligands, for the ligands under consideration [19]. Except for the position of NO^+, this series shows similarities with the ^{95}Mo shielding series, as also does the more tentative series of partial quadrupole splittings. These depend on the electric field gradient at the nucleus, so correlating with the ground state component of the paramagnetic term in nuclear magnetic shielding [2], and are found to decrease as $NO^+ > H^- > CO >$ *N*-ligands > *O*-ligands [19].

The position of NO^+ in the shielding series is thus a particularly interesting one. Although a strong ($\sigma + \pi$) ligand it appears low down in the ^{95}Mo series, and also in the ^{51}V series, in which the nitrosyls have about the same ^{51}V shielding as amines NR_3; corresponding results are obtained in ^{59}Co resonance [14]. The low position is related ultimately to the high electronegativity of nitrogen and oxygen: nephelauxetism is low and σ-donor ability reduced, while the $\pi^*(NO)$ orbital is sufficiently low-lying to mix substantially with the ligand field orbitals, so allowing the M–N=O group to bend at the ligating nitrogen, with transfer of a $d\pi$ electron pair to nitrogen as a lone pair [20] (as also for the diazenide and hydrazide(2 −) ligands [13]).

The ^{95}Mo shielding is sensitive to temperature changes, as evidenced by the shift of −776 ppm reported [21] for *trans*-$[Mo(N_2)_2(dptpe)_2]$ at 328 K, compared with our value of −793 at 298 K. Deshielding of transition metal nuclei with increase in temperature (of the order of 0.5 ppm per degree for metals of the second and third transition series) is commonly attributed to increase in accessibility of ligand field excited states, following the earlier theory [15]. More recent work, however, has shown the greater importance of bond extension at higher temperatures, as it affects ligand field splittings [22]; thus smaller temperature coefficients are observed for smaller rigid molecules than for larger flexible ones [11].

As an example of the lability of these complexes with increase in temperature, the shift we observed for *trans*-$[Mo(CO)_2(dppe)_2]$ of −1451 ppm, bearing the expected relation to that of the *cis* isomer (−1486 ppm) and related compounds, contrasts with the value of −1802 ppm reported for *trans*-$[Mo(CO)_2(dptpe)_2]$ in thf, determined at 330 K [21]; the difference from the shift for the dppe analogue should be 10 ppm or less. The −1802 ppm shift agrees with that reported [21] for *trans*-$[MoH_4(dptpe)_2]$, which may be formed from the *trans*-dicarbonyl if heated in thf [23], and with the value of -1865 ppm determined for *trans*-[$MoH_4(dppe)_2$] [24]. The fluxionality of this compound prevents the resolution of $^{95}Mo^{31}P$ spin–spin coupling. The ^{95}Mo shift given in Table 1 for freshly-prepared *trans*-[$Mo(CO)_2(dppe)_2$] corrects a reported value [7] which resembles that of the *cis* compound.

Spin–spin coupling

With adequate sensitivity the ^{95}Mo spectra of the dinitrogen compounds usually resemble simple multiplets, i.e. sextet, quintet, or quartet for $\{MoP_5\}$, $\{MoP_4\}$, or $\{MoP_3\}$ cores, respectively. This arises because of the breadth of the lines in ^{95}Mo resonance, and also the relatively small differences in $^1J(^{95}Mo^{31}P)$ values for non-equivalent phosphines. For *cis*-[$Mo(CO)_2(dppe)_2$], however, a more complex multiplet was obtained, showing the greater inequality of the $|^1J(^{95}Mo^{31}P)|$ values for phosphorus *trans* to phosphorus, or *trans* to carbonyl. It seems, therefore, that the *trans*-influences [25] on the $^1J(^{95}Mo^{31}P)$ coupling constants are more similar for N_2 and phosphines than for CO and phosphines. In *cis*-[$W(N_2)_2(Me_2Ph)_4$], also, rather similar $^1J(^{183}W^{31}P)$ values (309 and 313 Hz) were observed for the non-equivalent phosphines [26].

Similar $^1J(^{95}Mo^{31}P)$ values were observed for the chelating and unidentate phosphines. This is a general observation for five-membered chelate rings (although coupling constants are reduced in four-membered rings) [27]. $^1J(^{95}Mo^{31}P)$ is expected to be negative, as ^{95}Mo has a negative magnetic moment [28]. Absolute values of coupling constants normally increase with the electronegativity of substituents on either nucleus for a given bond type [25], as the Fermi contact term, which is the major contributor to the spin–spin coupling, is increased by increase in *p* character in the bonds, leaving greater *s* character at the nucleus, and increased also by *s* orbital contraction with increase in effective nuclear charge. Such effects are evident in the compounds in Table 1 in an increase in $|^1J(^{95}Mo^{31}P)|$ from CO to dinitrogen complexes, and from alkyl to arylphosphines.

The two PMe_3 complexes in Table 1 were about 50% labelled with $^{15}N_2$, so that $^{95}Mo^{15}N$ coupling was observable, with $|^1J(^{95}Mo^{15}N)|$ ca. 32 Hz. This compares with $|^1J(^{95}Mo^{14}N)|$ values of 40–45 Hz (equivalent to 56–63 Hz for ^{15}N) for the nitrosyl ligand in piano-stool complexes with cyclopentadienyl (etc.) co-ligands [29]. The larger value reflects the greater electronegativity of oxygen in NO than β-nitrogen in the NN ligand, and *trans* effects of the polyhapto ligand. There is also a sizeable isotope shift of 0.5 Hz to lower frequency for the ^{15}N- relative to the ^{14}N-containing complex, its magnitude reflecting the large shift range of the ^{95}Mo nucleus [30].

Experimental

The compounds were made by published methods [6,12,17,18,31], air-sensitive materials being handled by vacuum-line or Schlenk techniques under an atmosphere of dinitrogen or argon. All solvents were dried and freshly distilled under dinitrogen before use. ^{15}N-labelled complexes were made by exchange of the unlabelled complex with 95% $^{15}N_2$, and handled under argon [18].

The dinitrogen, diazenide, and hydrazide($2-$) complexes were made by published methods [1]. The *trans*-[$MoLL'(dppe)_2$] compounds were mostly made by exchange of L,L′ ligands, in overnight reactions in thf, with recrystallisation of each product. Thus *trans*-[MoBr(NO)(dppe)$_2$] was made from the hydrazido(2 −) compound *trans*-[MoBr(N$_2$H$_2$)(dppe)$_2$]Br by treatment with Me$_3$N and NO in thf [32], and *trans*-[Mo(NO)(NCMe)(dppe)$_2$] made from this by reaction with Tl[BF$_4$] in MeCN, then Na[BPh$_4$] in MeOH. This was converted to *trans*-[Mo(NO)(N$_3$)(dppe)$_2$] (by excess KN$_3$ in 1/1 thf/MeOH). *Trans*-[Mo(CO)$_2$(dppe)$_2$] was freshly made for NMR study by bubbling CO through a solution of *trans*-[Mo(CO)(NCC$_6$H$_4$OMe-4)(dppe)$_2$].

^{95}Mo spectra at 5.80 MHz were measured on a JEOL FX90Q spectrometer with external (^{7}Li) lock, typically with pulse repetition rates of 0.1 s, and pre-acquisition delays in excess of 200 μs to minimise effects of probe ringing; 90° pulses may be used without saturation.

^{95}Mo spectra at 26.08 MHz were measured on a Bruker WH400 spectrometer with pulse repetition rates up to 0.05 s (0.01 s for rapid accumulation). An example is an acquisition time of 0.017 s produced by a sweep width of 30 kHz (about 1000 ppm) in 1K data points. Only short pre-acquisition delays were required, in view of the short ring-down time of the low-frequency probe. Baseline distortion was removed by zeroing initial data points of the FID. FIDs were typically zero-filled up to 8 or 16 K before transformation.

^{95}Mo spectra at 23.46 MHz were run on a WM360 instrument with similar parameters to those used on the WH400, except that pre-acquisition delays of up to 600 μs were sometimes necessary because of the poor ring-down characteristics of the high *Q* factor broad-band VSP probe. The 90° pulse length was about 50 μs.

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