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Preliminary communication

PROPERTIES OF THE DINITROGEN LIGAND DEDUCED FROM ^{95}Mo NMR SPECTROSCOPY

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Summary

An NMR spectrochemical series (PF_3 ~ phosphite ~ CO > aryl phosphine > alkyl phosphine > MeCN > pyridine ~ piperidine > N_2 > NO) is apparent from the ^{95}Mo chemical shifts in octahedral (d^6) complexes containing these ligands. The $|^1J(^{95}\text{MoP})|$ spin—spin coupling constants contain information on the relative electron-donor abilities of the CO and N_2 ligands.

Direct NMR observation of ^{95}Mo is becoming more accessible [1—4], despite the quadrupole moment and low NMR sensitivity, and promises to be of value for the study of molybdoenzymes as well as of molybdenum complexes. We report measurements on dinitrogen and nitrosyl complexes of Mo^0 (d^6) which provide new information on the dinitrogen ligand, and extend the region reported for Mo^0 from δ −2100 [1] to −450 ppm.

Table 1 shows that *trans*-bis-dinitrogen complexes with two tetraaryldiphosphine (dppe) ligands have $\delta(^{95}\text{Mo})$ −785 (±12). Replacement of each tetraaryl (dppe) by a tetraalkyl diphosphine (depe) deshields molybdenum by 100 ppm, whereas replacement of dppe by four monodentate phosphines deshields molybdenum by 330 (±10) ppm, irrespective of stereochemistry. These relationships parallel those observed for carbonylphosphine complexes [3], for which the molybdenum resonances are some 700 ppm to higher field. In nitrosyl complexes with tetraaryldiphosphine coligands, however, molybdenum is somewhat deshielded, with δ around −500 ppm, and similar or lower molybdenum shieldings are found for dinitrosyls $[MoX_2(NO)_2L_2]$ [5].

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TABLE 1

^{95}Mo NMR PARAMETERS FOR DINITROGEN AND RELATED COMPLEXES

Compound	Solvent	δ (^{95}Mo)[a] (ppm)	$\|^1J(^{95}Mo^{31}P)\|$[b] (Hz)
$[Mo(CO)_6]$	CH_2Cl_2	−1855	185
cis-$[Mo(CO)_4(dppe)]$[c]	CH_2Cl_2	−1781	130
mer-$[Mo(CO)_3(triphos)]$[c]	CH_2Cl_2	−1759	129
cis-$[Mo(CO)_2(dppe)_2]$	thf	−1490	n.r.
cis-$[Mo(CO)_2(dArpe)_2]$[d]	thf	−1484	n.r.
Ar = C_6H_4OMe-4			
trans-$[Mo(CO)_2(dppe)_2]$	thf	−1465	n.r.
$[Mo(CO)_5(py)]$[e]	$CHCl_3$	−1387	—
cis-$[Mo(CO)_4(NCMe)_2]$[c]	MeCN	−1304	—
cis-$[Mo(CO)_4(bipy)]$[f]	dmf	−1190	—
cis-$[Mo(CO)_4(pip)_2]$[c]	dmf	−1093	—
trans-$[Mo(N_2)_2(depe)_2]$	thf	−1022	185
trans-$[Mo(N_2)_2(depe)(dppe)]$	thf	−899	185
trans-$[Mo(N_2)_2(dArpe)_2]$	thf		
Ar = C_6H_4OMe-4		−798	190
Ar = C_6H_4Me-3		−795	ca. 165
Ar = C_6H_4Me-4 (i.e. dpte)		−793	175
Ar = C_6H_5 (i.e. dppe)		−787	180
Ar = C_6H_4Cl-4		−785	180
Ar = $C_6H_4CF_3$-4		−774	180
trans-$[Mo(N_3)(NO)(dppe)_2]$	CH_2Cl_2	−614	n.r.
trans-$[Mo(NO)(NCMe)(dppe)_2](BF_4)$	CH_2Cl_2	−553	n.r.
trans-$[Mo(NO)(dppe)_2]$	CH_2Cl_2	−514	n.r.
trans-$[Mo(N_2)_2(PMePh_2)_4]$	thf	−464	190
trans-$[Mo(N_2)_2(PMe_2Ph)_4]$	thf	−447	n.r.

[a] Relative to external aqueous 2*M* sodium molybdate at pH 11.5, downfield positive, ± 1 ppm. The bis-dinitrogen complexes with depe or monodentate phosphines were measured at 5.8 MHz, those with dppe and substituted dppe ligands, and also the nitrosyls, at 26.08 MHz. Linewidths at half-height were 40—150 Hz. [b] ± 10 Hz. [c] Ref. 3. [d] (dArpe) is $Ar_2PCH_2CH_2PAr_2$. [e] Ref. 2. [f] Ref. 1b.

These results follow the patterns observed for other transition metals [6, 7], relatively high molybdenum shielding correlating with the low oxidation state, with octahedral coordination, and with the presence of relatively strong π-accepting ligands such as CO. The approximate ligand field theory of Griffith and Orgel [8], developed for d^6 octahedral complexes of cobalt, shows that the chemical shift of the metal is strongly influenced by $d\pi \rightarrow d\sigma^{\star}$ circulations of the electrons in the magnetic field, the deshielding being the larger the smaller is the ligand field splitting $\Delta E(t_{2g} \rightarrow e_g)$. Thus higher shielding is expected for ligands higher in the spectrophotochemical series. There is also an inverse dependence on the cube of the d-electron radius, so that higher shielding may be observed also for ligands with a large nephelauxetic effect, with effects also of covalency of the metal—ligand bond [5]. The spectrochemical series is sensitive to the σ-donor and π-acceptor ability of the ligand, the nephelauxetic series to the polarizability of the ligating atom [9]. The effects of polysubstitution show some additivity [1—3], but for complexes with mixed ligands, imbalance of charge in the valence shell of the metal and lifting of orbital degeneracy may decrease the shielding.

Our results confirm that ^{95}Mo shielding increases with replacement of a weaker by a stronger phosphine ligand, as in the substitution of aryl by alkyl groups on phosphorus. Within the group of complexes with tetraaryldiphosphine ligands the relative shifts are small, but higher ^{95}Mo shielding correlates with increased donor ability of the *para*-substituent of the aryl group (correlation coefficient 0.982 with the Hammett function σ_p, that with σ_p^+ being significantly less). $E^{ox}_{1/2}$ of these complexes, also, correlates with σ_p rather than with σ_p^+ [10].

Comparison with published data [2—4] shows that ^{95}Mo shielding decreases in the sequence PF_3 ~ phosphite ~ CO > phosphine > MeCN > pyridine ~ piperidine > N_2 > (linear) NO. This sequence bears an interesting resemblance to the spectrochemical series constructed from other evidence (notably from electronic, vibrational, and Mössbauer spectroscopy) [9, 11], placing N_2 and (linear) NO with the other nitrogen donor ligands. Relatively high shielding of the metal in octahedral (d^6) complexes with more polarizable ligating atoms, such as the heavier halogens, is observed for molybdenum [2, 3] as well as for other transition metals [6, 7]. The relatively low metal shielding with the (linear) NO ligand is observed also in vanadium and cobalt resonance [7, 12], but is unexpected on grounds of ligand field strength, nitrosyl being a fairly strong π-acceptor, and we are investigating this further.

Although resolution is often poor, the molybdenum—phosphorus coupling constants appear to be significantly larger in the dinitrogen than in corresponding carbonyl complexes. (They are probably negative, because of the negative magnetic moment of ^{95}Mo [13]). It is observed for all nuclei that absolute values of coupling constants (^1J or ^2J) increase with the electronegativity of the substituents on either nucleus (for given oxidation states and coordination numbers). This is explained by greater *p* character in the bonds to the electronegative substituents, leaving greater *s* character at the coupled nuclei [14], which (reinforced by the orbital contraction due to the increased effective nuclear charge) increases the Fermi contact spin—spin coupling term. Thus $|^1J(^{95}\text{MoP})|$ in $[Mo(CO)_5(phos)]$ complexes increases from 125 to 280 Hz in the sequence $PR_3 < PAr_3 < P(NMe_2)_3 < P(OR)_3 < PCl_3 < PF_3$ [3, 4]. The observed increase from 130 to ca. 180 Hz from carbonyl to dinitrogen coligands suggests a decrease from CO to N_2 in ability to transfer σ-electron density to molybdenum. This information, with that of the NMR spectrochemical series, usefully supplements the evidence from other physical measurements [11] on the ligating properties of dinitrogen.

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