Inorg. Chem. **1983**, *22*, 908-911

Contribution from the Departments of Chemistry, La Trobe University, Bundoora, Victoria 3083, Australia,
The University of Nebraska—Lincoln, Lincoln, Nebraska 68588, and CSIRO Division of Materials Science,
University of Melbourne, Parkville, Victoria 3052, Australia

Applications of ^{95}Mo NMR. 8.[1] Molybdenum(0) Carbonyl Derivatives of Phosphines, Phosphites, and Related Ligands

ANTHONY F. MASTERS,[2a,c] GERALD E. BOSSARD,[2b] T. ADRIAN GEORGE,[2b] ROBERT T. C. BROWNLEE,[2a] MAXWELL J. O'CONNOR,*[2a] and ANTHONY G. WEDD*[2a]

Received August 10, 1982

A series of mononuclear molybdenum(0) species [Mo(CO)$_6$], [Mo(CO)$_5$L], *cis*-[Mo(CO)$_4$L$_2$], and *fac*-[Mo(CO)$_3$L$_3$] (L = phosphine, phosphite, or a related ligand) exhibit ^{95}Mo NMR resonances in the range −1090 to −1870 ppm. For a given ligand L, there is a progressive downfield shift as substitution occurs in the above series and ^{95}Mo shielding increases with the atomic number of the group 5 donor atom: N < P < As < Sb. For phosphorus-based ligands, line widths are sufficiently narrow for characteristic ^{95}Mo–^{31}P coupling to be observed. In the binuclear anion [Mo$_2$(CO)$_{10}$H]$^-$, ^{95}Mo–^{1}H coupling is observed for the first time, $^1J(^{95}\text{Mo},^1\text{H})$ = 15 Hz. The dinitrogen complex *trans*-[Mo(N$_2$)$_2$(dptpe)$_2$] (dptpe = (*p*-tolyl)$_2$PCH$_2$CH$_2$P(*p*-tolyl)$_2$) exhibits a well-developed quintet at −776 ppm, the most shielded Mo(0) signal observed to date. It is apparent that the ^{95}Mo chemical shift cannot be used to distinguish, a priori, among mononuclear Mo(0), Mo(II), and Mo(IV) species but is highly sensitive to structural and electronic variations within a series of closely related mononuclear compounds.

Introduction

Recent reports[3-10] have highlighted the potential of ^{95}Mo NMR as a sensitive probe of electronic effects within organomolybdenum compounds. Despite the quadrupole moment associated with this nucleus ($I = {}^5/_2$, $Q \approx 0.011 \times 10^{-24}$ cm^2, 15.72 atom %), line widths are acceptably narrow in a large number of compounds, and this fact, together with rapid data accumulation, has prompted the recent work. The chemical shift range currently covers 7000 ppm for all molybdenum species, and minor structural changes can be easily detected. The chemical shift ranges observed for mononuclear molybdenum complexes to data are as follows: Mo(0), −1000 to −2200 ppm;[3,5-7,9,10] Mo(II), −100 to −2100 ppm;[3,4,6,8] Mo(IV), −300 to −3000 ppm;[11,12] Mo(VI), +3200 to −200 ppm.[13-19] Polynuclear species do not necessarily resonate in these ranges.[1]

The present paper concentrates on mononuclear molybdenum(0) compounds containing carbonyl and phosphorus-based ligands. It reports chemical shift and line width data and $^1J(^{95}\text{Mo},^{31}\text{P})$ coupling constants as well as the observation of ^{95}Mo–^{1}H coupling in [Mo$_2$(CO)$_{10}$H]$^-$ and a signal from a molecule containing coordinated dinitrogen. A preliminary note has appeared[3] as have two companion studies on (arene)tricarbonylmolybdenum(0)[5] and benzyltricarbonyl (η^5-cyclopentadienyl)molybdenum(II)[4] derivatives. Recent work by other groups on Mo(0) species is detailed in ref 6, 7, 9, and 10. In particular, some of the species used in the present work have also been examined in the other studies.[6,9]

Experimental Section

The substituted carbonyls were prepared in dry solvents under an atmosphere of dintriogen by using literature methods.[20-24] *fac*-[Mo(CO)$_3$(bpy)(P(OEt)$_3$)] (bpy = bipyridine, C$_{10}$H$_8$N$_2$) was obtained as red-purple crystals by refluxing 2 equiv of P(OEt)$_3$ with [Mo(CO)$_4$(bpy)] in toluene. It was characterized by elemental analysis (Anal. Calcd for C$_{19}$H$_{23}$N$_2$PO$_6$Mo: C, 45.43; H, 4.62; N, 5.58; P, 6.17. Found: C, 45.12; H, 4.56; N, 5.55; P, 6.4) and by ^{1}H NMR and infrared spectroscopy (ν_{CO} in CH$_2$Cl$_2$: 1928 s, 1828 m, 1792 m cm^{-1}). [MoH$_4$(dptpe)$_2$] and *trans*-[Mo(N$_2$)$_2$(dptpe)$_2$] (dptpe = (*p*-tolyl)$_2$PCH$_2$CH$_2$P(*p*-tolyl)$_2$) were prepared by a published method[25] while the carbonyl derivative [Mo(CO)$_2$(dptpe)$_2$] was obtained by passing carbon monoxide for 24 h at room temperature into a tetrahydrofuran solution (50 cm^3) containing *trans*-[Mo(N$_2$)$_2$(dptpe)$_2$] (0.8 g).

^{95}Mo NMR spectra were recorded by using the pulsed FT NMR technique at 6.5 MHz on a JEOL PFT100 spectrometer at 22 °C with a specifically tuned probe having an external ^{2}H$_2$O lock (10-mm sample tubes) or a JEOL FX 200 spectrometer equipped with a multinuclear probe at 13.0 MHz (15-mm sample tubes) at various temperatures. Solutions of the carbonyl compounds were approximately 0.3–0.5 M in molybdenum, and 3000 transients typically gave a signal to noise ratio of at least 60:1. The dptpe derivatives had maximum solubilities of about 0.15 M at 60 °C. The spectral bandwidths, repetition times, and number of pulses used in recording the spectra were as follows: *trans*-[Mo(N$_2$)$_2$(dptpe)$_2$], 10 kHz, 210 ms, 198 000; [MoH$_4$(dptpe)$_2$], 10 kHz, 225 ms, 158 000; [Mo(CO)$_2$(dptpe)$_2$], 20 kHz, 112 ms, 595 000.

Digital spectrometer resolution varied between 0.97 and 9.8 Hz/data point depending on the spectral bandwidth (2000–20000 Hz) and the

---

(1) For part 7, see: Gheller, S. F.; Hambley, T. W.; Brownlee, R. T. C.; O'Connor, M. J.; Snow, M. R.; Wedd, A. G. *J. Am. Chem. Soc.*, in press.

(2) (a) La Trobe University. (b) The University of Nebraska—Lincoln. (c) CSIRO Division of Materials Science.

(3) Masters, A. F.; Brownlee, R. T. C.; O'Connor, M. J.; Wedd, A. G.; Cotton, J. D. *J. Organomet. Chem.* **1980**, *195*, C17.

(4) Brownlee, R. T. C.; Masters, A. F.; O'Connor, M. J.; Wedd, A. G.; Kimlin, H. A.; Cotton, J. D. *Org. Magn. Reson.* **1982**, *20*, 73.

(5) Masters, A. F.; Brownlee, R. T. C.; O'Connor, M. J.; Wedd, A. G. *Inorg. Chem.* **1981**, *20*, 4183.

(6) Dysart, S.; Georgii, I.; Mann, B. E. *J. Organomet. Chem.* **1981**, *213*, C10.

(7) Minelli, M.; Rockway, T. W.; Enemark, J. H.; Brunner, H.; Muschiol, M. *J. Organomet. Chem.* **1981**, *217*, C34.

(8) Le Gall, S. Y.; Kubicki, M. M.; Petillon, F. Y. *J. Organomet. Chem.* **1981**, *221*, 287.

(9) Alyea, E. C.; Lenkinski, R. E.; Somogyvari, A. *Polyhedron* **1982**, *1*, 130.

(10) Bailey, J. T.; Clark, R. J.; Levy, G. C. *Inorg. Chem.* **1982**, *21*, 2085.

(11) Lee, R. K.; Howlader, N. C.; Haight, G. P.; Oldfield, E., submitted for publication.

(12) Gheller, S. F.; O'Connor, M. J.; Wedd, A. G., unpublished observations.

(13) Vold, R. R.; Vold, R. L. *J. Magn. Reson.* **1975**, *19*, 365.

(14) Kautt, W. D.; Kruger, H.; Lutz, O.; Maier, H.; Nolle, A. *Z. Naturforsch., A* **1976**, *31A*, 351.

(15) Lutz, O.; Nolle, A.; Kroneck, P. *Z. Naturforsch., A* **1976**, *31A*, 454–456; **1977**, *32A*, 505.

(16) Masters, A. F.; Gheller, S. F.; Brownlee, R. T. C.; O'Connor, M. J.; Wedd, A. G. *Inorg. Chem.* **1980**, *19*, 3866.

(17) Gheller, S. F.; Gazzana, P. A.; Masters, A. F.; Brownlee, R. T. C.; O'Connor, M. J.; Rodgers, J. R.; Snow, M. R.; Wedd, A. G. *Inorg. Chim. Acta* **1981**, *54*, L131.

(18) Christensen, K. A.; Muller, P. E.; Minelli, M.; Rockway, T. W.; Enemark, J. H. *Inorg. Chim. Acta* **1981**, *56*, L27.

(19) Freeman, M. A.; Schultz, F. A.; Reilley, C. N. *Inorg. Chem.* **1982**, *21*, 567.

(20) Magee, T. A.; Mathews, C. N.; Wang, T. S.; Wotiz, J. H. *J. Am. Chem. Soc.* **1961**, *83*, 3200.

(21) Todd, L. J.; Wilkinson, J. R. *J. Organomet. Chem.* **1974**, *77*, 1.

(22) Darensbourg, D. J.; Kump, R. L. *Inorg. Chem.* **1978**, *17*, 2680.

(23) Darensbourg, D. J.; Brown, T. L. *Inorg. Chem.* **1968**, *7*, 959.

(24) Pidcock, A.; Smith, J. D.; Taylor, B. W. *J. Chem. Soc. A* **1967**, 872.

(25) Archer, L. J.; George, T. A. *Inorg. Chem.* **1979**, *18*, 2079.

0020-1669/83/1322-0908$01.50/0

Table I. ^{95}Mo NMR Data at 22 °C for Carbonyl Derivatives

compd	solvent	δ(^{95}Mo)	$W_{h/2}$,[b] Hz	^1J(^{95}Mo,^{31}P), Hz
$[Mo(CO)_6]$	CH_2Cl_2	−1857	4	
$Et_4N[HMo_2(CO)_{10}]$	THF	−1937	30	15[c]
$[Mo(CO)_5(PEt_3)]$	*a*	−1857	15	133
	CH_2Cl_2	−1856	6	131
$[Mo(CO)_5(P\text{-}n\text{-}Bu_3)]$	*a*	−1842	41	133
$[Mo(CO)_5(PPh_3)]$	CH_2Cl_2	−1743	35	144
$[Mo(CO)_5(AsPh_3)]$	$CHCl_3$	−1751	153	
$[Mo(CO)_5(SbPh_3)]$	$CHCl_3$	−1865	186	
$[Mo(CO)_5(PMe_2Ph)]$	$CHCl_3$	−1788	8	131
$[Mo(CO)_5(PEt_2Ph)]$	CH_2Cl_2	−1815	11	132
$[Mo(CO)_5(P\text{-}n\text{-}Bu_2Ph)]$	CH_2Cl_2	−1808	19	133
$[Mo(CO)_5(P(OMe)_3)]$	*a*	−1864	5	218
$[Mo(CO)_5(P(OEt)_3)]$	*a*	−1854	8	214
$[Mo(CO)_5(P(O\text{-}i\text{-}Pr)_3)]$	*a*	−1835	15	215
$[Mo(CO)_5(P(O\text{-}n\text{-}Bu)_3)]$	*a*	−1854	29	216
$[Mo(CO)_5(P(OPh)_3)]$	$CHCl_3$	−1819	51	237
$[Mo(CO)_4(bpy)]$	DMF	−1190	110	
cis-$[Mo(CO)_4(PEt_3)_2]$	CH_2Cl_2	−1764	22	125
cis-$[Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2]$	CH_2Cl_2	−1743	34	124
cis-$[Mo(CO)_4(P\text{-}n\text{-}Bu_2Ph)_2]$	CH_2Cl_2	−1688	76	140
cis-$[Mo(CO)_4(Ph_2PCH_2PPh_2)]$	CH_2Cl_2	−1552	159	119
cis-$[Mo(CO)_4(Ph_2P(CH_2)_2PPh_2)]$	CH_2Cl_2	−1782	46	145
cis-$[Mo(CO)_4(Ph_2P(CH_2)_3PPh_2)]$	CH_2Cl_2	−1694	61	142
cis-$[Mo(CO)_4(P(OMe)_3)_2]$	CH_2Cl_2	−1828	11	215
cis-$[Mo(CO)_4(P(OEt)_3)_2]$	CH_2Cl_2	−1807	13	213
cis-$[Mo(CO)_4(P(O\text{-}i\text{-}Pr)_3)_2]$	CH_2Cl_2	−1762	21	209
cis-$[Mo(CO)_4(P(O\text{-}n\text{-}Bu)_3)_2]$	CH_2Cl_2	−1808	29	212
cis-$[Mo(CO)_4(P(OPh)_3)_2]$	CH_2Cl_2	−1752	50	226
fac-$[Mo(CO)_3(P\text{-}n\text{-}Bu_3)_3]$	CH_2Cl_2	−1521	10	124
fac-$[Mo(CO)_3(P(OMe)_3)_3]$	CH_2Cl_2	−1756	5	214
fac-$[Mo(CO)_3(P(OEt)_3)_3]$	CH_2Cl_2	−1721	4	210
fac-$[Mo(CO)_3(bpy)(P(OEt_3)_2]$	CH_2Cl_2	−1097	53	240

[a] The solvent is the ligand. [b] Line width corrected for applied line broadening (normally 1–50 Hz). [c] ^1J(^{95}Mo,^{1}H).

Table II. ^{95}Mo NMR Data for dptpe Derivatives

compd	solvent	T, °C	δ	^1J(^{95}Mo,^{31}P), Hz	$W_{h/2}$,[a] Hz
trans-$[Mo(N_2)_2(dptpe)_2]$	THF	55	−776	205	85[b]
$[MoH_4(dptpe)_2]$	toluene	65	−1805	*c*	350
$[Mo(CO)_2(dptpe)_2]$	THF	57	−1802	*c*	121
			−1475	*c*	207

[a] Line widths corrected for applied line broadening of 50–100 Hz. [b] Average apparent line width of the three central components of the quintet. Total line broadening applied over the quintet was 60 Hz. [c] Incompletely resolved multiplets: δ measured at center of envelope.

number of data points (4096 or 8192) employed. All line widths [$W_{h/2}$ (Hz)] have been corrected for exponential line broadening. Chemical shifts in parts per million are referred to external aqueous 2 M Na_2MoO_4 at pH 11. Bulk susceptibility corrections are negligible.

Results and Discussion

^{95}Mo chemical shifts, coupling constants and line widths are collected in Tables I and II. The majority of the present range of compounds are $[M(CO)_5P]$, *cis*-$[Mo(CO)_4P_2]$, and *fac*-$[Mo(CO)_3P_3]$ derivatives (Table I) where P is a phosphorus ($I = {}^1/_2$)-based ligand. Such species are expected[26] to have relatively small electric field gradients at the molybdenum nucleus, and the observed narrow line widths (<50 Hz) suggest that the quadrupolar contribution to the line width is minimal in these species. The broader lines observed for certain compounds can be traced in each case to the presence of unresolved scalar coupling to (quadrupolar) ligand nuclei (^{14}N, ^{75}As, ^{121}Sb, ^{123}Sb) or to reduced symmetry at the molybdenum nucleus with a consequent enhancement of the quadrupolar contribution to the line width.

The Species [Mo(CO)$_5$L]. When L is PR_3 or $P(OR)_3$, single 1:1 doublets are observed (Figure 1a) in the range −1740 to −1865 ppm (δ −1857 for $[Mo(CO)_6]$). Within this range the introduction of phenyl substituents does lead to some deshielding.

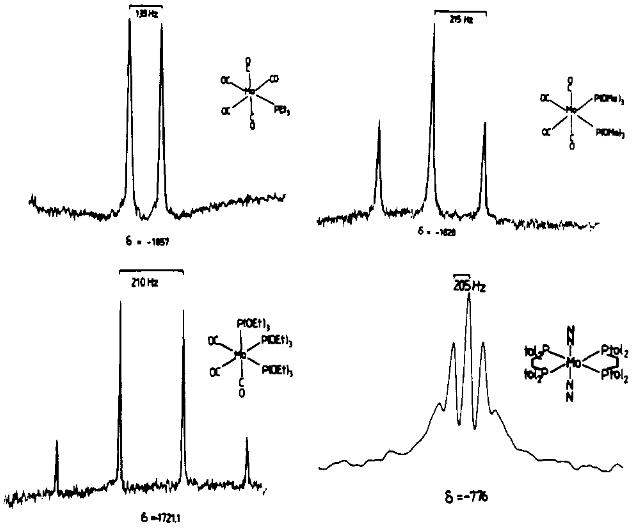

Figure 1. ^{95}Mo NMR spectra of (a) $[Mo(CO)_5(PEt_3)_2]$, (b) *cis*-$[Mo(CO)_4(P(OMe)_3)_2]$, (c) *fac*-$[Mo(CO)_3(P\text{-}n\text{-}Bu_3)_3]$, and (d) *trans*-$[Mo(N_2)_2(dptpe)_2]$.

The available data (Table I; ref 6, 9) for substituted carbonylmolybdenum(O) species indicates that ^{95}Mo shielding increases with the atomic number of group 5 donor atoms: N < P < As < Sb. A comparison of ^{51}V and ^{95}Mo shielding in

---

(26) Yamasaki, A.; Yajima, F.; Fujiwara, S. *Inorg. Chim. Acta* **1968**, *2*, 39.

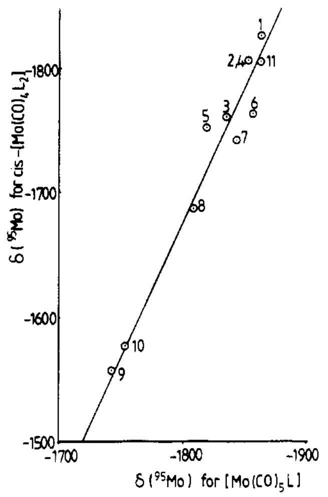

Figure 2. Correlation between $\delta(^{95}Mo)$ for *cis*-[Mo(CO)$_4$L$_2$] and [Mo(CO)$_5$L] for L = (1) P(OMe)$_3$, (2) P(OEt)$_3$, (3) P(O-*i*-Pr)$_3$, (4) P(O-*n*-Bu)$_3$, (5) P(OPh)$_3$, (6) PEt$_3$, (7) P-*n*-Bu$_3$, (8) PBu$_2$Ph, (9) PPh$_3$, (10) AsPh$_3$, and (11) SbPh$_3$.

the isoelectronic species [V(CO)$_5$(EPh$_3$)]$^-$[27] and [Mo(CO)$_5$(EPh$_3$)] (E = P, As, Sb) shows the same order; the considerably increased shielding for the SbPh$_3$ derivative (Table I) is noteworthy. This order contrasts with that observed[17] for group 6 donors bound to mononuclear molybdenum(VI): Se < S < O, N. A more complete understanding of donor atom effects and their underlying origins must await carefully designed experimental and theoretical study.

The coupling constants $^1J(^{95}Mo,^{31}P)$ are conveniently derived from the ^{95}Mo NMR spectra. Extraction from ^{31}P NMR spectra[19] is complicated by overlap of the satellite peaks (^{95}Mo, 15.72 atom %, $I = {}^5/_2$, μ −0.9133 μ_N; ^{97}Mo, 9.46 atom %, $I = {}^5/_2$, μ −0.9325 μ_N (μ_N = nuclear magneton)) due to the near-equivalence of $^1J(^{95}Mo,^{31}P)$ and $^1J(^{97}Mo,^{31}P)$. However, good agreement is observed between values obtained from observation of either nucleus. Changing from a phosphine to the analogous phosphite increases $^1J(^{95}Mo,^{31}P)$ by 60–70% (130–150 Hz vs. 210–240 Hz), which parallels the behavior of many metal complex systems.[28a] There is a linear relation between $^1J(^{95}Mo,^{31}P)$ and $^1J(^{183}W,^{31}P)$ for the species [M(CO)$_5$PR$_3$] (M = Mo, W) for existing data (Table I; ref 28b: 9 examples), which indicate that common effects are operating. In particular, the suggested correlation between a shorter W–P bond distance and a higher $^1J(^{183}W,^{31}P)$ coupling constant in the compounds [W(CO)$_5$(PPh$_3$)] and [W(CO)$_5$(P(OPh)$_3$] may carry over into the molybdenum systems as suggested by comparison of metal–phosphorus coupling contants:

[Mo(CO)$_5$(PPh$_3$)]	144 Hz	[W(CO)$_5$(PPh$_3$)]	280 Hz
[Mo(CO)$_5$(P(OPh)$_3$]	237 Hz	[W(CO)$_5$(P(OPh)$_3$)]	411 Hz

The same order obtains for the P-*n*-Bu$_3$ and P(O-*n*-Bu)$_3$ derivatives.

The Species *cis*-[Mo(CO)$_4$L$_2$]. When L is PR$_3$ or P(OR)$_3$, simple 1:2:1 triplets are observed (Figure 1b) downfield of the corresponding [Mo(CO)$_5$L] signal. There is a correlation between the respective chemical shifts (Figure 2: 11 examples) which extends to the AsPh$_3$ and SbPh$_3$ derivatives.

In the chelated species *cis*-[Mo(CO)$_4$(Ph$_2$P(CH$_2$)$_n$PPh$_2$)], an intriguing variation in the shielding of the ^{95}Mo nucleus with *n* is observed and the order is opposite to that observed for the ^{31}P nucleus:[28d]

$$^{95}\text{Mo: } n = 1 < 3 < 2 \qquad ^{31}\text{P: } n = 1 > 3 > 2$$

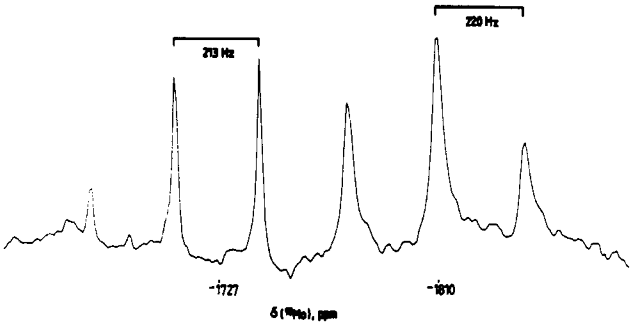

Figure 3. ^{95}Mo NMR spectrum of the products of the reaction of *fac*-[Mo(CO)$_3$(bpy)(P(OEt)$_3$)] with P(OEt)$_3$ (see text).

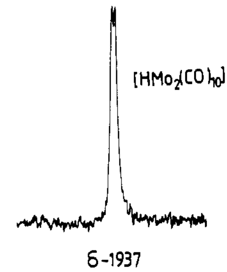

Figure 4. ^{95}Mo NMR spectrum of Et$_4$N[Mo$_2$(CO)$_{10}$H] in THF.

The same trends are observed[29] for the ^{51}V and ^{31}P chemical shifts in the series *cis*-[V(CO)$_4$(Ph$_2$P(CH$_2$)$_n$PPh$_2$)]$^-$ and [HV(CO)$_4$(Ph$_2$P(CH$_2$)$_n$PPh$_2$)], which are isoelectronic with the molybdenum compounds. While the data for the vanadium series have been correlated[29] with parameters such as bond angles and π-bonding effects, it is fair to say that the origins of the metal and phosphorus[28e] shielding trends remain obscure.

Coupling constants $^1J(^{95}Mo,^{31}P)$ and line widths are very similar for the series *cis*-[Mo(CO)$_4$L$_2$] and [Mo(CO)$_5$L]. A broader line and a smaller coupling constant are observed for *cis*-[Mo(CO)$_4$(Ph$_2$PCH$_2$PPh$_2$)] than for *cis*-[Mo(CO)$_4$(Ph$_2$P(CH$_2$)$_n$PPh$_2$)] (n = 2, 3). The P–Mo–P bond angle of 67.3° in the former compound suggests[30] a strained system. Unless ligand-exchange processes are induced, the increased line width would be related to an effectively lower symmetry at the molybdenum nucleus.

The Species *fac*-[Mo(CO)$_3$L$_3$]. For the limited number of species examined with L = PR$_3$ or P(OR)$_3$, simple 1:3:3:1 quartets (Figure 1c) are observed and downfield from the corresponding *cis*-[Mo(CO)$_4$L$_2$] and [Mo(CO)$_5$L] compounds, a trend confirmed[6,9] for L = MeCN, pyridine, AsPh$_3$, and SbPh$_3$. Again, ^{95}Mo shielding increases with the atomic number of the donor atom.

The chemical shift, −1097 ppm, for *fac*-[Mo(CO)$_3$(bpy)P(OEt$_3$)] illustrates the marked deshielding effect of nitrogen donor atoms in these species. The combined effects of lower symmetry and unresolved scalar coupling to ^{14}N presumably lead to the increase in line width of the observed doublet, compared to those of the other *fac* isomers reported here. The potential of using ^{95}Mo NMR to monitor reactions in these systems is illustrated by Figure 3: when *fac*-[Mo(CO)$_3$(bpy)(P(OEt)$_3$] reacts with neat P(OEt)$_3$), two products can be detected: *fac*-[Mo(CO)$_3$(P(OEt)$_3$)$_3$] (quartet, δ −1727, $^1J(^{95}Mo,^{31}P)$ = 213 Hz) and *cis*-[Mo(CO)$_4$(P(OEt)$_3$)$_2$] (triplet, δ −1810, $^1J(^{95}Mo,^{31}P)$ = 220 Hz).

---

[27] Rehder, D. *Chem. Ber.* **1978**, *111*, 1978. $\delta(^{51}V)$, relative to VOCl$_3$ in CHCl$_3$ (1:2 v/v), for [V(CO)$_5$(EPPh$_3$)]$^-$: E = P, −1790; E = As, −1800; E = Sb, −1890.

[28] (a) Pregosin, R. S.; Kunz, R. W. *NMR: Basic Prin. Prog.* **1979**, *16*, 21; (b) *Ibid.* **1979**, *16*, 99; (c) *Ibid.* **1979**, *16*, 25; (d) *Ibid.* **1979**, *16*, 133; (e) *Ibid.* **1979**, *16*, 54.

[29] Rehder, D. *J. Magn. Reson.* **1980**, *38*, 419.

[30] Cheung, K. K.; Lai, T. F.; Mok, K. J. *J. Chem. Soc. A* **1971**, 1644.

$Et_4N[Mo_2(CO)_{10}H]$. This binuclear anion resonates (Table I, Figure 4) at high field as expected for a formally Mo(0) species. ^{95}Mo–^{1}H coupling, $^1J(^{95}Mo,^1H)$ = 15 Hz, is observed directly and was confirmed by proton decoupling.

***trans*-$[Mo(N_2)_2(dptpe)_2]$ and Related Species.** It was necessary to heat these systems above room temperature in order to detect resonances under the present conditions. The observation (Table II, Figure 1d) of a quintet for *trans*-$[Mo(N_2)_2(dptpe)_2]$ in tetrahydrofuran (THF) under dinitrogen at 55 °C confirms a trans configuration with four equivalent phosphorus atoms. The integrity of the solution was monitored by infrared spectroscopy[25] at room temperature before and after the measurement. In addition, ^{15}N NMR measurements[31] confirm the stability of $[Mo(N_2)_2(PR_3)_4]$ species in THF under argon at 30 °C. The ^{95}Mo chemical shift of −776 ppm for this compound is the lowest field signal yet observed for a formally Mo(0) species and further illustrates the large deshielding effect of nitrogen donors. Interestingly, $^1J(^{95}Mo,^{31}P)$, 205 Hz, is larger than expected on the basis of comparisons with the other systems studied. The chemical shift range for Mo(0) is now −776 to −2200 ppm, and an extension to lower field can be expected as more nitrogen-containing species are examined. Examination of the chemical shift ranges presented in the Introduction make it apparent that the ^{95}Mo chemical shift cannot be used to distinguish among mononuclear species of Mo(0), Mo(II), and Mo(IV). However, the shift is highly sensitive to structural and electronic variations within a closely related series of mononuclear compounds, as illustrated in previous work[4,5,9] and in Table I.

A solution obtained by treating *trans*-$[Mo(N_2)_2(dptpe)_2]$ in THF with CO for 24 h showed two incompletely resolved multiplets at −1802 and −1475 ppm, which suggest the presence of *cis*- and *trans*-$[Mo(CO)_2(dptpe)_2]$. The tetrahydride $[MoH_4(dptpe)]$ in toluene at 65 °C exhibited a broad resonance at −1805 ppm: ^{95}Mo–^{1}H and ^{95}Mo–^{31}P coupling was not observed, almost certainly due to intramolecular exchange processes which have been observed with such species by ^{1}H NMR.[25]

Acknowledgment. We thank Professors J. H. Enemark, G. P. Haight, Jr., G. C. Levy, and E. Oldfield for preprints of results. The Australian Research Grants Scheme and the Australian Wool Corp. are thanked for generous support of this work.

Registry No. ^{95}Mo, 14392-17-7; $[Mo(CO)_6]$, 13939-06-5; $Na[HMo_2(CO)_{10}]$, 84417-20-9; $[Mo(CO)_5(PEt_3)]$, 19217-79-9; $[Mo(CO)_5(P(n\text{-}Bu)_3)]$, 15680-62-3; $[Mo(CO)_5(PPh_3)]$, 14971-42-7; $[Mo(CO)_5(AsPh_3)]$, 19212-22-7; $[Mo(CO)_5(SbPh_3)]$, 19212-21-6; $[Mo(CO)_5(PMe_2Ph)]$, 24554-78-7; $[Mo(CO)_5(PEt_2Ph)]$, 72868-87-2; $[Mo(CO)_5(P(n\text{-}Bu)_2Ph)]$, 18534-33-3; $[Mo(CO)_5(P(OMe)_3)]$, 15631-20-6; $[Mo(CO)_5(P(OEt)_3)]$, 15603-75-5; $[Mo(CO)_5(P(OPr\text{-}i)_3)]$, 34369-19-2; $[Mo(CO)_5(P(OBu\text{-}n)_3)]$, 21485-22-3; $[Mo(CO)_5(P(OPh)_3)]$, 15711-66-7; $[Mo(CO)_4(bpy)]$, 15668-64-1; *cis*-$[Mo(CO)_4(PEt_3)_2]$, 19217-80-2; *cis*-$[Mo(CO)_4(P(n\text{-}Bu)_3)_2]$, 16244-54-5; *cis*-$[Mo(CO)_4(P(n\text{-}Bu)_2Ph)_2]$, 29825-19-2; *cis*-$[Mo(CO)_4(Ph_2PCH_2PPh_2)]$, 26743-81-7; *cis*-$[Mo(CO)_4(Ph_2P(CH_2)_2PPh_2)]$, 15444-66-3; *cis*-$[Mo(CO)_4(Ph_2P(CH_2)_3PPh_2)]$, 15553-68-1; *cis*-$[Mo(CO)_4(P(OMe)_3)_2]$, 15631-22-8; *cis*-$[Mo(CO)_4(P(OEt)_3)_2]$, 38604-20-5; *cis*-$[Mo(CO)_4(P(OPr\text{-}i)_3)_2]$, 84472-14-0; *cis*-$[Mo(CO)_4(P(OBu\text{-}n)_3)_2]$, 84472-15-1; *cis*-$[Mo(CO)_4(P(OPh)_3)_2]$, 59599-01-8; *fac*-$[Mo(CO)_3(P(Bu\text{-}n)_3)_3]$, 29825-20-5; *fac*-$[Mo(CO)_3(P(OMe)_3)_3]$, 15631-24-0; *fac*-$[Mo(CO)_3(P(OEt)_3)_3]$, 38542-39-1; *fac*-$[Mo(CO)_3(bpy)(P(OEt)_3)]$, 84472-16-2; *trans*-$[Mo(N_2)_2(dptpe)_2]$, 70320-87-5; $[MoH_4(dptpe)_2]$, 70320-86-4; $[Mo(CO)_2(dptpe)_2]$, 84417-21-0.

---

[31] Chatt, J.; Fakley, M. E.; Richards, R. L.; Mason, J.; Stenhouse, I. A. *J. Chem. Res., Synop.* **1979**, 44.

Contribution from the Department of Chemistry,
University of Nottingham, Nottingham, England NG7 2RD

Mixed Carbonyl–Dinitrogen Compounds: Synthesis and Thermal Stability of $Cr(CO)_{6-x}(N_2)_x$ in Liquid-Xenon Solution and Low-Temperature Matrices

JAMES J. TURNER,* MICHAEL B. SIMPSON, MARTYN POLIAKOFF, WILLIAM B. MAIER II,[1a]
and MICHAEL A. GRAHAM[1b]

Received April 14, 1982

The mixed carbonyl–dinitrogen species of Cr, $Cr(CO)_{6-x}(N_2)_x$ (x = 1–5), have been generated by UV photolysis of $Cr(CO)_6$ in liquid Xe/N_2 mixtures, at 183 K. The product species are identified by IR spectroscopy and characterized on the basis of photochemical behavior, and thermal stability, by comparison with simple theoretical arguments of predicted IR band intensity and position. Further detailed identification is also achieved by selective narrow-band photolysis at 367 nm, which distinguishes between cis/trans and *mer*/*fac* isomers of $Cr(CO)_4(N_2)_2$ and $Cr(CO)_3(N_2)_3$, respectively. Comparison is also made with matrix isolation experiments, including isotopic ($C^{18}O$) substitution. The molecule $Cr(CO)_5N_2$ is found to be thermally stable in solution in liquid xenon at −35 °C, whereas the most highly N_2-substituted species $Cr(CO)(N_2)_5$ is thermally unstable at −90 °C.

I. Introduction

The matrix isolation technique has proved extremely valuable for the structural characterization of coordinatively *unsaturated* species such as $Cr(CO)_5$[2] and $Fe(CO)_4$.[3] It has also, however, proved its value in characterizing unstable coordinatively *saturated* species such as $Ni(N_2)_4$,[4] $Pd(CO)_4$,[5] and $Ni(CO)_3N_2$.[6,7] Recently, we have shown[8] that some of these saturated species may be spectroscopically examined following photochemical generation using *liquid* noble-gas

---

[1] (a) Present address: Los Alamos National Laboratory, Los Alamos, NM 87545. (b) Present address: Perkins Engines Ltd., Eastfield, Peterborough, UK.

[2] (a) Graham, M. A.; Poliakoff, M.; Turner, J. J. *J. Chem. Soc. A* **1971**, 2939–2948. (b) Perutz, R. N.; Turner, J. J. *Inorg. Chem.* **1975**, *14*, 262–270.

[3] Poliakoff, M.; Turner, J. J. *J. Chem. Soc., Dalton Trans.* **1974**, 2276–2285.

[4] Huber, H.; Kundig, E. P.; Moskovits, M.; Ozin, G. A. *J. Am. Chem. Soc.* **1973**, *95*, 332.

[5] Darling, J. H.; Ogden, J. S. *Inorg. Chem.* **1972**, *11*, 666.

[6] Kundig, E. P.; Moskovits, M.; Ozin, G. A. *Can. J. Chem.* **1973**, *51*, 2737.

[7] Rest, A. J. *J .Organomet. Chem.* **1972**, *40*, C76.

[8] (a) Maier II, W. B.; Poliakoff, M.; Simpson, M. B.; Turner, J. J. *J. Chem. Soc., Chem. Commun.* **1980**, 587. (b) Maier II, W. B.; Poliakoff, M.; Simpson, M. B.; Turner, J. J. *J. Mol. Struct.* **1982**, *80*, 83.

0020-1669/83/1322-0911$01.50/0