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^{95}Mo NMR SPECTRAL STUDIES ON SEVEN-COORDINATE MOLYBDENUM(II) ISOCYANIDE COMPLEXES

MARTIN MINELLI, J.H. ENEMARK*
Department of Chemistry, University of Arizona, Tucson, Arizona 85721 (U.S.A.)

ANDREW BELL and RICHARD A. WALTON*
Department of Chemistry, Purdue University, West Lafayette, Indiana 47907 (U.S.A.)

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Summary

The ^{95}Mo NMR spectra of a series of seven-coordinate molybdenum(II) isocyanide complexes of the types $[Mo(CNR)_{7-n}L_n](PF_6)_2$ (R = CH_3, $CHMe_2$, CMe_3, C_6H_{11}, CH_2Ph; L = py, bpy, Me_2bpy, phen, dppe, $P\text{-n-Bu}_3$; $n = 0,1,2$) $[Mo(CNCMe_3)_6X]PF_6$ (X = Cl, Br, I) and $[\{Mo(CNCMe_3)_4(N\text{-}N)\}_2(\mu\text{-CN})](PF_6)_3$ (N–N = bpy, Me_2bpy, phen) have been studied. The ^{95}Mo chemical shift range for this group of complexes is about 1100 ppm. An increase in the size of the R group attached to the isocyanide ligand generally tends to shield the ^{95}Mo nucleus. Replacement of the isocyanide ligand with a phosphorus ligand also increases the shielding, whereas the replacement of isocyanide with a heterocyclic nitrogen donor leads to deshielding by 800–900 ppm. This group of complexes shows a normal halogen dependence, i.e. replacement of Cl^- by Br^- and I^- increases the shielding of the ^{95}Mo nucleus. The cyano-bridged cations $[\{Mo(CNCMe_3)_4(N\text{-}N)\}_2(\mu\text{-CN})]^{3+}$ (N–N = bpy, Me_2bpy, or phen) show two ^{95}Mo NMR signals, one for the molybdenum coordinated to the carbon of the bridging CN and one for the *N*-coordinated molybdenum. Comparison of the chemical shifts and linewidths of the cyano-bridged species with those of the corresponding mononuclear molybdenum(II) complexes $[Mo(CNCMe_3)_5(N\text{-}N)](PF_6)_2$ leads to the assignment of the more deshielded signal to the *N*-coordinated molybdenum. The ^{14}N and ^{31}P NMR spectra for these complexes have also been measured, as have the ^{13}C NMR spectra of the pairs of complexes $[Mo(CNCMe_3)_5(N\text{-}N)](PF_6)_2$ and $[\{Mo(CNCMe_3)_4(N\text{-}N)\}_2(\mu\text{-CN})](PF_6)_3$ (N–N = bpy or phen). The ^{183}W NMR spectra for $[W(CNR)_5(bpy)](PF_6)_2$ (R = CMe_3 and CH_2Ph), show that the $\delta(^{183}W)/\delta(^{95}Mo)$ chemical shift ratios for isocyanide complexes are different from the ratio found for M^0 and M^{VI}.

Introduction

The use of ^{95}Mo NMR spectroscopy to characterize diamagnetic molybdenum compounds in solution has expanded rapidly in recent years [1]. Dioxomolybdenum(VI) compounds [2], molybdenum(0) pentacarbonyl compounds [3], and molybdenum dinitrosyl compounds [4] have been studied extensively. Within each series large chemical shifts are observed upon systematic substitution of ligands. However, a given ligand does not produce the same chemical shift response in each series of compounds. For example, replacement of 2,4-pentanedione (acac) by dithiocarbamate (dtc) in the pair $MoO_2(acac)_2$ and $MoO_2(dtc)_2$ results in an increase of 172 ppm [2a] in the ^{95}Mo chemical shift. On the other hand for the pair $Mo(NO)_2(acac)_2$ to $Mo(NO)_2(dtc)_2$ the chemical shift decreases by 132 ppm [4].

To date no ^{95}Mo NMR spectra have been reported for molybdenum complexes containing more than one isocyanide ligand. The ready availability of a range of homoleptic isocyanide complexes of molybdenum(II) of the type $[Mo(CNR)_7]X_2$ as well as their substitution products $[Mo(CNR)_{7-n}L_n]X_2$, where $n = 1$ or 2, containing a variety of tertiary phosphine and nitrogen (heterocyclic tertiary amine) donors (L) [5–11], has afforded us an ideal and timely opportunity to undertake a study of the chemical shift response of molybdenum(II) isocyanide complexes. The only other groups of organometallic molybdenum(II) complexes which have been studied to date are diastereomeric complexes of the type $CpMo(CO)_2(NN^*)$, where (NN^*) is a chiral bidentate ligand [12], and complexes of the type $CpMo(CO)_3X$ [13]. As far as studies on other molybdenum(II) complexes are concerned, only the quadruply bonded dimolybdenum(II) carboxylates $Mo_2(O_2CR)_4$, where R = CF_3 or n-Pr, have been investigated by ^{95}Mo NMR spectroscopy [14].

Of additional interest to us was the possibility of using ^{95}Mo NMR spectroscopy to differentiate the two chemically distinct molybdenum(II) environments in the novel cyano-bridged species $[\{Mo(CNCMe_3)_4(N\text{–}N)\}_2(\mu\text{-}CN)]X_3$ (N–N = bpy, Me_2bpy or phen) [11]. Our success in doing this points the way for the further application of ^{95}Mo NMR spectroscopy in unravelling other structural problems of this kind.

The present report describes the results of a ^{95}Mo NMR spectral study of these molybdenum(II) isocyanide complexes as well as some related ^{13}C, ^{14}N, and ^{31}P NMR spectral data.

Experimental section

Starting materials. The following compounds were prepared by standard literature procedures: methyl isocyanide [15], isopropyl isocyanide [16], iodobenzene dichloride ($PhICl_2$) [17], $Mo(CO)_4$bpy [18], and $Mo(CO)_3(HgCl)(bpy)Cl$ [19]. The compounds 2,2′-bipyridine (bpy), 4,4′-dimethyl-2,2′-bipyridine (Me_2bpy), and $Mo(CO)_6$ were obtained from commercial sources as were all other reagents and solvents.

General reaction procedures. All reactions were carried out under a nitrogen atmosphere, and solvents were dried over molecular sieves and deoxygenated by purging with N_2 gas prior to use. In general, KPF_6 was added to the reaction mixtures, where the reacting species started as their PF_6^- salts, to prevent formation of products containing the $H_2PO_4^-$ counter anion.

Preparation of seven-coordinate molybdenum(II) isocyanide complexes

The following compounds $[Mo(CNR)_7](PF_6)_2$ (R = CMe_3 and C_6H_{11}) [20], $[Mo(CNCMe_3)_6Cl]PF_6$ [21], $[Mo(CNR)_5(bpy)](PF_6)_2$ (R = CMe_3, C_6H_{11} and CH_2Ph) [22], $[Mo(CNR)_5(phen)](PF_6)_2$ (R = CMe_3 and C_6H_{11}) [22], $[\{Mo(CNCMe_3)_4(N-N)\}_2(\mu-CN)](PF_6)_3$ (N–N = bpy and Me_2bpy) [11], $[Mo(CNR)_5(dppe)](PF_6)_2$ (R = CMe_3 and C_6H_{11}) [7], $[Mo(CNCMe_3)_6(P\text{-}n\text{-}Bu_3)](PF_6)_2$ [7], and $[Mo(CNCMe_3)_6(py)](PF_6)_2$ [11] were prepared as reported in the literature. The complexes $[Mo(CNCMe_3)_6X]PF_6$ (X = Br^- and I^-) were prepared from $[Mo(CNCMe_3)_6Cl]PF_6$ by anion–ligand exchange with the appropriate potassium salt in refluxing ethanol.

Several new complexes of the preceding types were prepared for the first time in the present study, while some known complexes were prepared by alternative procedures.

(i) $[Mo(CNCH_3)_5(bpy)](PF_6)_2$. This complex was synthesized by a modification of the method described in ref. 22. A saturated solution of $Mo(CO)_4$bpy (1.0 g, 2.75 mmol) in 60 ml of deoxygenated methanol contained in a three-necked flask was stirred at room temperature and then treated with $PhICl_2$ (1.15 g, 4.18 mmol). Immediately following this addition, a quantity of CH_3NC (0.92 ml, 16.5 mmol) was syringed into the reaction mixture whereupon its color changed from pale yellow to dark red-orange. The resulting solution was stirred at room temperature for an additional 16 h, and then filtered into a KPF_6/acetone solution (1.0 g of KPF_6 in 10 ml of acetone). The volume of this solution was reduced under a stream of nitrogen gas, and the dark red-orange powder that precipitated was collected by filtration and washed with water, methanol, and diethyl ether. The product was recrystallized from methanol; yield 0.41 g (20%). Anal. Found: C, 30.94; H, 3.15. $C_{20}H_{23}F_{12}MoN_7P_2$ calcd. C, 32.15; H, 3.08%. IR spectrum: ν(C≡N) 2242m, 2213sh, 2186sh, 2151s, and 2139s cm^{-1}; ν(C=N) of bpy 1603m cm^{-1}. Electronic absorption spectrum (methanol): 518 nm (ϵ 4800 M^{-1} cm^{-1}), and 340 nm (ϵ 7400 M^{-1} cm^{-1}). ^1H NMR spectrum (acetone-d_6): δ(ppm) 3.72 (15H, s, CH_3NC), 7.78 (2H, triplet of doublets (td), bpy), 8.31 (2H, td, bpy), 8.70 (2H, d, bpy), and 9.19 (2H, d, bpy). Cyclic voltammetry (0.2 *M* TBAH/CH_2Cl_2): $E_{p,a}$ +1.15, $E_{1/2}$ +0.81, and $E_{p,c}$ −1.22 V vs. SCE.

(ii) The formation of $[Mo(CNCMe_3)_5(bpy)](PF_6)_2$ by the reaction of $Mo(CO)_3(HgCl)(bpy)Cl$ with t-butyl isocyanide. A quantity of $Mo(CO)_3(HgCl)(bpy)Cl$ (0.6 g, 0.99 mmol) was stirred for 30 min at room temperature in 50 ml of deoxygenated methanol in a three-necked flask. The addition of t-butyl isocyanide (0.625 ml, 5.9 mmol) to the pale orange methanolic solution changed its color to a dark orange-red. The resulting reaction mixture was stirred for 4 h at room temperature, and the dark red solution was then filtered into a KPF_6/acetone solution (1.0 g KPF_6 in 15 ml acetone). A small quantity of light gray material (shown to be $HgCl_2$) and elemental mercury (0.32 g) remained on the filter. The volume of the resulting solution was reduced under a stream of nitrogen gas, and the dark red crystalline product, $[Mo(CNCMe_3)_5(bpy)](PF_6)_2$, that precipitated was collected by filtration and washed with water and diethyl ether. The product was recrystallized from a methanol/diethyl ether mixture (2/1); yield 0.52 g (60%). The product was found by infrared and ^1H NMR spectroscopies, and cyclic voltammetry to be identical to an authentic sample of $[Mo(CNCMe_3)_5(bpy)](PF_6)_2$ [11].

(iii) $[Mo(CNCHMe_2)_5(bpy)](PF_6)_2$. This dark red-orange complex was obtained

by a procedure analogous to that described in section (ii) using Mo(CO)$_3$(HgCl)(bpy)Cl (1.33 g, 2.19 mmol) and isopropyl isocyanide (1.05 ml, 11.54 mmol) in 50 ml of methanol; yield 1.26 g (65%). Anal. Found: C, 40.32; H, 4.60. $C_{30}H_{43}F_{12}MoN_7P_2$ calcd.: C, 40.59; H, 4.85%. IR spectrum: ν(C≡N) 2201m, 2170s, 2130s, 2110s and 2035m cm^{-1}; ν(C=N) of bpy 1604m cm^{-1}. Electronic absorption spectrum (methanol): 516 nm (ϵ 4600 M^{-1} cm^{-1}) and 338 nm (ϵ 7600 M^{-1} cm^{-1}). ^{1}H NMR spectrum (acetone-d_6): δ(ppm) 1.38 (30H, d, CNCH(C*H*$_3$)$_2$), 4.40 (5H, spt, CNC*H*(CH$_3$)$_2$), 7.86 (2H, td, bpy), 8.35 (2H, td, bpy) 8.77 (2H, d, bpy), and 9.18 (2H, d, bpy). Cyclic voltammetry (0.2 M TBAH/CH$_2$Cl$_2$): $E_{p,a}$ +1.62, $E_{1/2}$ +0.87, and $E_{p,c}$ −1.22 V vs. SCE.

(iv) [Mo(CNCMe$_3$)$_4$(Me$_2$bpy)Cl]PF$_6$. A mixture of [{Mo(CNCMe$_3$)$_4$(Me$_2$bpy)}$_2$(μ-CN)](PF$_6$)$_3$ (0.85 g, 0.505 mmol), KPF$_6$ (0.3 g, 1.63 mmol), and Me$_3$CCl (15 ml, 0.138 mol) was refluxed in methanol (25 ml) for 8 h. The purple solution was cooled to 0°C and filtered and the filtrate taken to dryness under a stream of nitrogen. The purple powder was washed with water and diethyl ether and dried in vacuo. The resulting complex [Mo(CNCMe$_3$)$_4$(Me$_2$bpy)Cl]PF$_6$ was recrystallized from an acetone/diethyl ether mixture (1/2) and then from a dichloromethane/diethyl ether mixture (1/2); yield 0.65 g (82%). Anal. Found: C, 48.84; H, 6.14. $C_{32}H_{48}ClF_6MoN_6P$ calcd.: C, 48.46; H, 6.06%. IR spectrum: ν(C≡N) 2153s, 2089s and 2053s cm^{-1}; ν(C=N) of Me$_2$bpy 1619m cm^{-1}. Electronic absorption spectrum (methanol): 518 nm (ϵ 4800 M^{-1} cm^{-1}) and 341 nm (ϵ 5100 M^{-1} cm^{-1}). ^{1}H NMR spectrum (acetone-d_6): δ(ppm) 1.56 (36H, s, CNCMe$_3$), 2.55 (6H, s, *Me*$_2$bpy), 7.51 (2H, d, Me$_2$bpy), 8.46 (2H, s, Me$_2$bpy), and 8.98 (2H, d, Me$_2$bpy). Cyclic voltammetry (0.2 M TBAH/CH$_2$Cl$_2$): $E_{p,a}$ +1.35, $E_{1/2}$ +0.43, and $E_{p,c}$ −1.79 V vs. SCE.

(v) [Mo(CNCMe$_3$)$_5$(Me$_2$bpy)](PF$_6$)$_2$. A mixture of [Mo(CNCMe$_3$)$_4$(Me$_2$bpy)Cl]PF$_6$ (0.60 g, 0.757 mmol) and KPF$_6$ (0.25 g, 1.36 mmol) in 30 ml of deoxygenated methanol were warmed gently until the solids dissolved. The addition of t-butyl isocyanide (0.1 ml, 0.947 mmol) to the resulting solution caused the purple solution to change color immediately to a dark red-orange. The reaction mixture was heated for 1 h, cooled to 0°C, and the volume of the solution reduced under a stream of nitrogen gas. The dark red-orange crystalline product obtained was collected by filtration, washed with water and diethyl ether. A portion of the product was recrystallized from a methanol/diethyl ether mixture (1/2); yield 0.66 g (88%). Anal. Found: C, 44.42; H, 5.95. $C_{37}H_{57}F_{12}MoN_7P_2$ calcd.: C, 45.08; H, 5.79%. IR spectrum: ν(C≡N) 2184m, 2145s, 2122s, and 2050sh cm^{-1}; ν(C=N) of Me$_2$bpy 1619m cm^{-1}. Electronic absorption spectrum (methanol): 502 nm (ϵ 5000 M^{-1} cm^{-1}) and 333 nm (ϵ 7200 M^{-1} cm^{-1}). ^{1}H NMR spectrum (acetone-d_6): δ(ppm) 1.52 (45H, s, CNCMe), 2.63 (6H, s, *Me*$_2$bpy), 7.72 (2H, d, Me$_2$bpy), 8.65 (2H, s, Me$_2$bpy) and 8.93 (2H, d, Me$_2$bpy). Cyclic voltammetry (0.2 M TBAH/CH$_2$Cl$_2$): $E_{p,a}$ +1.67, $E_{1/2}$ +0.85 and $E_{p,c}$ −1.33 V vs. SCE.

(vi) [{Mo(CNCMe$_3$)$_4$(phen)}$_2$(μ-CN)](PF$_6$)$_3$. A mixture of [Mo(CNCMe$_3$)$_5$(phen)](PF$_6$)$_2$ (1.0 g, 1.02 mmol) and KPF$_6$ (0.5 g, 2.72 mmol) in 30 ml of 1-propanol was heated at reflux for 20 h. The solution was cooled to 0°C and filtered, and the dark red powder was washed with copious amounts of water, diethyl ether, and hexane before drying in vacuo. The product was recrystallized several times from a dichloromethane/diethyl ether mixture (1/2); yield 0.63 g (73%). The spectroscopic and electrochemical properties of this compound were identical with those exhibited by an authentic sample of [{Mo(CNCMe$_3$)$_4$(phen)}$_2$(μ-CN)](PF$_6$)$_3$ [11].

Physical measurements

IR spectra of Nujol mulls were recorded in the region 4000–400 cm^{-1} on an IBM Instruments IR/32 Fourier transform spectrometer. Routine ^{1}H NMR spectra were recorded using a Perkin–Elmer R-32 90MHz spectrometer. Resonances were referenced internally, usually to the residual protons in the incompletely deuterated solvents. Electronic absorption spectra were recorded on methanolic solutions using an IBM instruments 9420 UV-visible spectrophotometer. Cyclic voltammetry measurements were performed as discussed in previous work [23].

The proton decoupled ^{13}C NMR spectra were recorded on acetone-d_6 or acetonitrile-d_3 solutions using a Varian XL-200 spectrometer. Resonances were referenced internally to TMS, and 0.02 M $Cr(acac)_3$ was used as a relaxation agent. The remaining NMR spectra (^{95}Mo, ^{31}P and ^{14}N) were obtained using a Bruker WM 250 NMR spectrometer. Acetone, distilled from P_2O_5 prior to use, was used as solvent, the concentrations were approximately 5×10^{-2} M. For the ^{95}Mo NMR spectra a molybdenum probe (16.3 MHz) was used. To reduce the effects of probe ringing a Doty Scientific duplexer and pre-amplifier with a 16 MHz center was inserted between the probe and the Bruker broadband pre-amplifier. The duplexer was gated off during the pulse and for 15 μsec after the pulse. With this arrangement the acquisition delay was reduced to 100 μsec. A 2 M $NaMoO_4$ solution in D_2O, effective pH 11, was used as external standard. In the case of the ^{31}P NMR spectral measurements, the decoupling coil (101 MHz) from the fixed molybdenum probe (16.3 MHz) was used. Concentrated phosphoric acid served as standard. The ^{14}N spectra were measured at 18.1 MHz with a digitally selected broadband probe (12.3–101 MHz), using the same experimental arrangement described above for molybdenum. The chemical shifts are relative to neat nitromethane. The ^{183}W NMR spectra were measured at 10.28 MHz using the same digitally selected broad-band probe, and the chemical shifts are reported relative to WO_4^{2-}.

Elemental microanalyses were performed by Dr. H.D. Lee of Purdue University microanalytical laboratory.

Results and discussion

The range of mixed alkyl isocyanide-bidentate *N*-heterocycle complexes of molybdenum(II) [11,22] has been expanded in the present investigation in order to make available for the NMR spectral study as varied a group of complexes as possible. In the course of this work we have developed a third method for preparing complexes of the type $[Mo(CNR)_5(N{-}N)](PF_6)_2$, viz., the reaction of the molybdenum(II) complex $Mo(CO)_3(HgCl)(bpy)Cl$ with RNC, followed by anion exchange using KPF_6 [24].

While the ^{1}H NMR spectra of the complexes $[Mo(CNR)_5(N{-}N)](PF_6)_2$ and $[\{Mo(CNR)_4(N{-}N)\}_2(\mu\text{-}CN)](PF_6)_3$ have been the subject of previous studies [11,22], it is appropriate here, for future discussions, to summarize very briefly certain conclusions. In acetone-d_6, the ^{1}H NMR spectra of $[Mo(CNR)_5(N{-}N)](PF_6)_2$ are consistent with the presence of normal chelating N–N ligands and reveal no inequivalences between the resonances attributable to the five RNC ligands over the temperature range −20 to +120°C. This is in accord with the expected fluxionality of such seven-coordinate species, as is apparently the case for the $[Mo(CNR)_7]^{2+}$ cations [5b], and various phosphine substituted derivatives thereof [7]. For the complexes $[\{Mo(CNR)_4(N-N)\}_2(\mu\text{-}CN)](PF_6)_3$, the ^1H NMR spectra of the coordinated N–N ligands can be interpreted [11,22] in terms of one of two possibilities: either two different bidentate ligands (i.e. those bound to two inequivalent Mo atoms) or the presence of inequivalent halves of two essentially identical bidentate ligands. The latter possibility need be considered because this is the situation found in the solid state based upon a crystal structure determination on $[\{Mo(CNCMe_3)_4(bpy)\}_2(\mu\text{-}CN)](PF_6)_3$ [11]. Although the cyano-bridged complexes where N–N = bpy or Me_2bpy show a single t-butyl proton resonance, the related phen derivative shows this resonance as a doublet [22]. We attribute this splitting to the magnetic inequivalence of the sets of Me_3CNC ligands that are bound to the inequivalent Mo atoms; in the case of the related bpy and Me_2bpy complexes such a splitting is simply not resolved.

Clearly then, if the RNC ligands on each Mo atom are rendered equivalent yet there is no process that leads to the exchange of ligands between the two ends of the molecule, then this is perhaps the best explanation as to why we see two sets of N–N ligand resonance [11,22].

In order to examine further this property, we have recorded the ^{13}C NMR spectra of the pairs of complexes $[Mo(CNCMe_3)_5(N-N)](PF_6)_2$ and $[\{Mo(CNCMe_3)_4(N-N)\}_2(\mu\text{-}CN)](PF_6)_3$, where N–N = bpy or phen. The appropriate data are available in Table S1 (Supplementary material). Resonances attributable to all the carbon atoms within the four complexes were readily assignable, including that of the μ-CN group ($\delta \sim 174$ ppm), through a comparison with previous literature data [5b,25–29]. Again we see evidence for inequivalency between the two bpy and phen ligands since there is a doubling of certain of the carbon ring resonances e.g. C(13), C(14) and C(5), C(6) of $[\{Mo(CNCMe_3)_4(phen)\}_2(\mu\text{-}CN)](PF_6)_3$ (see Table S1). Unfortunately, these data do not permit us to decide between the two possible explanations that have been advanced (vide supra), so that further discussion is inappropriate at this time, other than to reiterate that while fluxionality exists within the coordination spheres of the two Mo atoms, each retains its separate identity.

In this the first ^{95}Mo NMR spectral study of seven-coordinate molybdenum(II) isocyanide complexes (see Table 1, Fig. 1), we find a chemical shift range of about 1100 ppm, from +69 to −1003 ppm, occupying the more deshielded part of the known molybdenum(II) range (−100 to −2072 ppm according to ref. 30). The molybdenum chemical shifts appear to depend on the alkyl group of the isocyanide ligand, where the order of chemical shifts with alkyl groups is $CH_3 < CMe_3 < CHMe_2 < C_6H_{11} < CH_2C_6H_5$. This trend is observed for the series of mixed isocyanide-nitrogen heterocyclic ligand (bpy, Me_2bpy, and phen) complexes, for the homoleptic complex ($R = CMe_3$ and C_6H_{11}), and when two isocyanide ligands are replaced by a chelating dppe ligand (Table 1).

When one isocyanide ligand is substituted by a phosphine ligand the shielding increases by 10 ppm; two phosphines cause a shielding increase of 20 ppm for $R = CMe_3$ and 33 ppm for $R = C_6H_{11}$. This ^{95}Mo NMR chemical shift response upon phosphine substitution contrasts with that of $Mo(CO)_6$ (−1856 ppm in THF) [3a], where deshielding by 13 ppm occurs upon substitution of one CO by phosphine and deshielding of 74 ppm when two carbonyl groups are replaced by two phosphines.

The chemical shift of molybdenum(II) isocyanide complexes is especially sensitive to the introduction of heterocyclic nitrogen ligands. Conversion of $[Mo(CNCMe_3)_7]^{2+}$ to $[Mo(CNCMe_3)_5(bpy)]^{2+}$ (bpy = 2,2′-bipyridine) results in deshielding of the molybdenum nucleus by about 900 ppm. Further evidence of the unusual sensitivity of the ^{95}Mo NMR chemical shift of molybdenum(II) isocyanide complexes to the presence of such nitrogen donors is provided by the data in Table 2 showing the effect of replacing two phosphorus atoms by a bpy ligand in three classes of compounds. For the pair $[Mo(CNCMe_3)_5(dppe)]^{2+}$ and $[Mo(CNCMe_3)_5(bpy)]^{2+}$, the chemical shift difference is about 920 ppm. This difference is several hundred ppm larger than the chemical shift differences observed for the pairs $Mo(NO)_2Cl_2(PPh_3)_2$–$Mo(NO)_2Cl_2(bpy)$ and $Mo(CO)_4(dppe)$–$Mo(CO)_4(bpy)$ (Table 2). The complex $[Mo(CNCMe_3)_6Cl]PF_6$ resonates at −668 ppm. Replacement of the coordinated Cl^- by Br^- and I^- leads to more shielding of the ^{95}Mo nucleus, i.e. these isocyanide complexes show a normal halogen dependence [31]. The same

TABLE 1

CHEMICAL SHIFT DATA FOR ISOCYANIDE COMPLEXES OF MOLYBDENUM(II)[a]

Compound	$\delta(^{95}Mo)$[b] (ppm)	Line-width (Hz)	$\delta(^{31}P)$[c] (ppm)	Line-width (Hz)	$\delta(^{14}N)$[d] (ppm)	Line-width (Hz)
$[Mo(CNCMe_3)_7](PF_6)_2$	−960	35	–	–	−156	20
$[Mo(CNC_6H_{11})_7](PF_6)_2$	−970	70	–	–	−168	20
$[Mo(CNCMe_3)_6Cl]PF_6$	−688	450	–	–	−162	50
$[Mo(CNCMe_3)_6Br]PF_6$	−703	450	–	–	−161	30
$[Mo(CNCMe_3)_6I]PF_6$	−795	500	–	–	−160	40
$[Mo(CNCMe_3)_6(P\text{-}n\text{-}Bu_3)](PF_6)_2$	−970	300	36	50	−157	40
$[Mo(CNCMe_3)_6(py)](PF_6)_2$	−508	600	–	–	−157	40
$[Mo(CNCMe_3)_5(dppe)](PF_6)_2$	−980	600	66	55	−157	40
$[Mo(CNC_6H_{11})_5(dppe)](PF_6)_2$	−1003	1100	68	45	−168	50
$[Mo(CNCH_3)_5(bpy)](PF_6)_2$	−19	130	–	–	−186	60
$[Mo(CNCHMe_2)_5(bpy)](PF_6)_2$	−64	120	–	–	−159	30
$[Mo(CNCMe_3)_5(bpy)](PF_6)_2$	−57	100	–	–	−150	40
$[Mo(CNC_6H_{11})_5(bpy)](PF_6)_2$	−68	200	–	–	−161	100
$[Mo(CNCH_2Ph)_5(bpy)](PF_6)_2$	−115	220	–	–	−174	120
$[Mo(CNCMe_3)_5(Me_2bpy)](PF_6)_2$	−86	140	–	–	−150	40
$[Mo(CNCMe_3)_5(phen)](PF_6)_2$	−78	130	–	–	−150	30
$[Mo(CNC_6H_{11})_5(phen)](PF_6)_2$	−98	260	–	–	−161	60
$[\{Mo(CNCMe_3)_4(bpy)\}_2(\mu\text{-}CN)](PF_6)_3$	+69	360	–	–	−150	140
	−61	220				
$[\{Mo(CNCMe_3)_4(Me_2bpy)\}_2(\mu\text{-}CN)](PF_6)_3$	+46	320	–	–	−150	140
	−92	200				
$[\{Mo(CNCMe_3)_4(phen)\}_2(\mu\text{-}CN)\}(PF_6)_3$	+55[e]	200	–	–	−150	50
	−85[e]	100				

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[a] All compounds measured in acetone at room temperature unless stated otherwise. (See footnote *e*). We use the convention that negative chemical shifts are upfield (more shielded) and positive chemical shifts are downfield (more deshielded) relative to the external standard. [b] Chemical shift relative to 2 *M* Na_2MoO_4 in H_2O pH 11. [c] Chemical shift relative to phosphoric acid; PF_6^- shows up as a septet (central peak −143 ppm; *J* 700Hz). [d] Chemical shift of isocyanide nitrogen relative to external, neat nitromethane. [e] Measured in CH_3CN.

TABLE 2. ^{95}Mo CHEMICAL SHIFT DATA FOR RELATED CARBONYL, NITROSYL AND ISOCYANIDE COMPLEXES

Compound	Solvent	Chem. shift δ(ppm)	Linewidth (Hz)	Diff. Δδ(ppm)	Ref.
$Mo(CO)_5(P\text{-}n\text{-}Bu_3)$	CH_2Cl_2	−1843	20	456	3c
$Mo(CO)_5(py)$	$CDCl_3$	−1387	70		3c
$[Mo(CNCMe_3)_6(P\text{-}n\text{-}Bu_3)](PF_6)_2$	acetone	−970	300	462	[a]
$[Mo(CNCMe_3)_6(py)](PF_6)_2$	acetone	−508	600		[a]
$Mo(NO)_2Cl_2(PPh_3)_2$	DMF	−500	530	237	4
$Mo(NO)_2Cl_2(bpy)$	DMF	−263	170		4
$Mo(CO)_4(dppe)$	CH_2Cl_2	−1782	50	592	3i
$Mo(CO)_4(bpy)$	DMF	−1190	110		3i
$[Mo(CNCMe_3)_5(dppe)](PF_6)_2$	acetone	−980	600	923	[a]
$[Mo(CNCMe_3)_5(bpy)](PF_6)_2$	acetone	−57	100		[a]

[a] This work.

response to halogen exchange has been found for other molybdenum(II) complexes such as $CpMoX(CO)_3$ [13] and metal–metal quadruply bonded dimolybdenum(II) complexes [32].

The dimolybdenum(II) complexes $[\{Mo(CNCMe_3)_4(N\text{-}N)\}_2(\mu\text{-}CN)](PF_6)_3$ (N–N = bpy, Me_2bpy, or phen), show two distinct ^{95}Mo NMR signals, separated by 130 to 140 ppm (Fig. 2). A comparison of these signals with the corresponding data for $[Mo(CNCMe_3)_5(N\text{-}N)](PF_6)_2$ (N–N = bpy, Me_2bpy, or phen) leads to the assignment of the more shielded signal to the molybdenum atom bound to the C atom of the bridging CN group and of the relatively deshielded signal to the *N*-bound molybdenum. This result is in accord with the ^{1}H and ^{13}C NMR spectra discussed previously, in that two ^{95}Mo resonances are expected since there is no process that, on the NMR time scale, leads to an equivalence of the two molybdenum environments.

The colors of the molybdenum(II) isocyanide complexes range from yellow to dark burgundy [11,22]. However, in contrast to the previously studied series of *cis*-$Mo(CO)_4$(P-donor ligand)$_2$ complexes [3k] and dioxomolybdenum(VI)-Schiff base complexes [2d], there is no correlation between the molybdenum chemical shift and the energy of the first electron transition.

In the ^{14}N NMR spectra (Table 1), the isocyanide nitrogens are readily detected

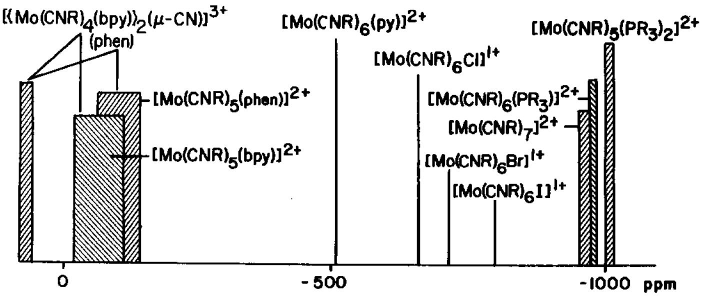

Fig. 1. ^{95}Mo chemical shift range for molybdenum(II) isocyanide complexes.

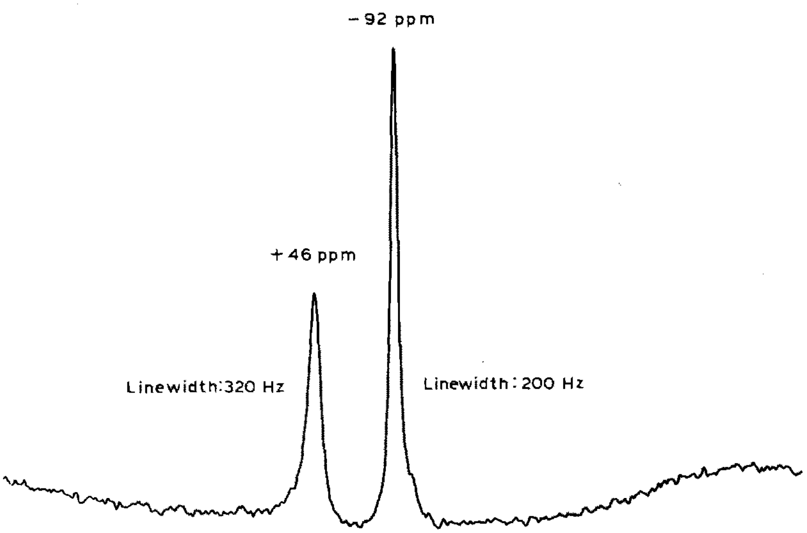

Fig. 2. ^{95}Mo NMR spectrum of [{Mo(CNCMe$_3$)$_4$(Me$_2$bpy)}$_2$(μ-CN)](PF$_6$)$_3$ in acetone.

and occur within the range expected for isocyanide ligands bound to metals [33]. A small shielding effect can be seen with an increase in the size of the R groups.

The ^{183}W NMR spectra for [W(CNCH$_2$Ph)$_5$(bpy)](PF$_6$)$_2$(−1193 ppm, 10 Hz) and [W(CNCMe$_3$)$_5$(bpy)](PF$_6$)$_2$(−1131 ppm, 10 Hz) have also been measured. A comparison of the ^{183}W and ^{95}Mo NMR data shows that the chemical shift ratio $\delta(^{183}W)/\delta(^{95}Mo) = 1.7$ which has been found by other authors [34,35] for a number of molybdenum and tungsten complexes, does not hold for these complexes. The $\delta(^{183}W)/\delta(^{95}Mo)$ ratios found here are 1.3 (M(CO)$_6$ as reference) [34] and 10–20 (MO_4^{2-} as reference) [35].

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Supplementary material available

Table S1 containing the ^{13}C NMR spectral data for [Mo(CNCMe$_3$)$_5$(N–N)](PF$_6$)$_2$ and [{Mo(CNCMe$_3$)$_4$(N–N)}$_2$(μ-CN)](PF$_6$)$_3$, where N–N = bpy or phen (1 page). This table is available from the authors upon request.

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