that $-\sigma_I$ increases with the basicity of the axial ligand, L, indicating that an increase in electron density placed on cobalt leads to an increase in the effect, supporting the hyperconjugation structures of eq 9. This is in direct contrast to the fluorophenylcobaloximes where $-\sigma_R{}^\circ$ (as an indicator of direct conjugation of cobalt with the aryl group) was found to decrease with increasing electron density on cobalt. It is also of interest to note that in Table VI changing L from Cl^- to I^- has very little effect on the measured ^{19}F NMR shifts and hence on the calculated values of σ_I for the $CH_2Co(D_2H_2)L$ substituents. Since I^- is known to interact with some aryl groups via involvement of unoccupied acceptor d orbitals,[5] such d-orbital interactions evidently do not occur with the cobalt atom in such complexes or they do not substantially effect the stability of the hyperconjugation structures of eq 9.

It should, finally, be pointed out that Bromilow et al.[33] have recently firmly demonstrated that the resonance effect of a given substituent, X, in a para-disubstituted benzene depends on the nature of the para detecting group Y and have suggested substitution of eq 10 (dual substituent parameter nonlinear

$$P = \sigma_I\rho_I + \sigma_R{}^\circ\rho_R/(1 - \epsilon\sigma_R{}^\circ) \qquad (10)$$

resonance effects or DSP–NLR) for the simpler eq 1 (dual substituent parameter or DSP) for para-disubstituted benzenes. In this equation, ϵ is treated as a fit parameter to be maximized for each data set and to allow for such nonlinear resonance effects. However, these authors have applied this approach to para-substituted fluorobenzene ^{19}F NMR chemical shifts and obtained a maximized value of 0.21 for ϵ. Application of eq 10 to the present data using this value of ϵ shows that the nonlinear resonance effect is extremely minor for para-substituted fluorobenzenes. This treatment caused no change whatsoever (to three significant figures) in any of the values of σ_I reported herein for cobaloxime-chelated cobalt centers and caused only minor changes in the calculated $\sigma_R{}^\circ$ values (in the third significant figure). Hence, while such nonlinear resonance effects are undoubtedly extremely important in some cases,[33] they are a very minor effect in the current case.

Acknowledgment. This research was supported by the Robert A. Welch Foundation, Houston, Texas (Grant Y-749), and, in part, by the National Science Foundation (Grant CHE78-18723, South Carolina Magnetic Resonance Laboratory). We are grateful to Dr. Ben Shoulders, The University of Texas at Austin, and to Dr. Paul D. Ellis and Dr. Ruth Inners, South Carolina Magnetic Resonance Laboratory, for their kind assistance in obtaining the ^{19}F NMR spectra.

Registry No. *m*-$FC_6H_4Co(D_2H_2)OH_2$, 78965-43-2; *p*-$FC_6H_4Co(D_2H_2)OH_2$, 57104-73-1; *m*-$FC_6H_4Co(D_2H_2)OH^-$, 78965-44-3; *p*-$FC_6H_4Co(D_2H_2)OH^-$, 78965-45-4; *m*-$FC_6H_4Co(D_2H_3)OH_2{}^+$, 78965-46-5; *p*-$FC_6H_4Co(D_2H_3)OH_2{}^+$, 78965-47-6; *m*-$FC_6H_4Co(D_2H_3)Cl$, 78965-48-7; *p*-$FC_6H_4Co(D_2H_3)Cl$, 78965-49-8; *m*-$FC_6H_4Co(D_2H_2)Me_2SO$, 78965-50-1; *p*-$FC_6H_4Co(D_2H_2)Me_2SO$, 78965-51-2; *m*-$FC_6H_4Co(D_2H_2)$(4-cyanopyridine), 78965-52-3; *p*-$FC_6H_4Co(D_2H_2)$(4-cyanopyridine), 78965-53-4; *m*-$FC_6H_4Co(D_2H_2)$(4-(carboxamido)pyridine), 78965-54-5; *p*-$FC_6H_4Co(D_2H_2)$(4-(carboxamido)pyridine), 78965-55-6; *m*-$FC_6H_4Co(D_2H_2)$(pyridine), 78965-56-7; *p*-$FC_6H_4Co(D_2H_2)$(pyridine), 42194-70-7; *m*-$FC_6H_4Co(D_2H_2)$(4-methylpyridine), 78965-57-8; *m*-$FC_6H_4Co(D_2H_2)$(4-aminopyridine), 78965-58-9; *p*-$FC_6H_4Co(D_2H_2)$(4-aminopyridine), 78965-59-0; *m*-$FC_6H_4Co(D_2H_2)$(glycine ethyl ester), 78965-60-3; *p*-$FC_6H_4Co(D_2H_2)$(glycine ethyl ester), 78965-61-4; *m*-$FC_6H_4Co(D_2H_2)$(2,2-dimethoxyethylamine), 78965-62-5; *p*-$FC_6H_4Co(D_2H_2)$(2,2-dimethoxyethylamine), 78965-63-6; *m*-$FC_6H_4Co(D_2H_2)$(2-methoxyethylamine), 78965-64-7; *p*-$FC_6H_4Co(D_2H_2)$(2-methoxyethylamine), 78965-65-8; *m*-$FC_6H_4Co(D_2H_2)$(*n*-propylamine), 78965-66-9; *p*-$FC_6H_4Co(D_2H_2)$(*n*-propylamine), 78965-67-0; *m*-$FC_6H_4Co(D_2H_2)$(*S*-methyl-2-mercaptoethanol), 78965-68-1; *p*-$FC_6H_4Co(D_2H_2)$(*S*-methyl-2-mercaptoethanol), 78965-69-2; *m*-$FC_6H_4Co(D_2H_2)$(methyl *S*-methylmercaptoacetate), 78965-70-5; *p*-$FC_6H_4Co(D_2H_2)$(methyl *S*-methylmercaptoacetate), 78965-71-6; *m*-$FC_6H_4Co(D_2H_2)$(triphenylphosphine), 78965-72-7; *p*-$FC_6H_4Co(D_2H_2)$(triphenylphosphine), 78965-73-8; *m*-$FC_6H_4Co(D_2H_2)$(methyl mercaptoacetate), 78965-74-9; *p*-$FC_6H_4Co(D_2H_2)$(methyl mercaptoacetate), 78965-75-0; *m*-$FC_6H_4Co(D_2H_2)$(methyl mercaptopropionate), 78965-76-1; *p*-$FC_6H_4Co(D_2H_2)$(methyl mercaptopropionate), 78965-77-2; *m*-$FC_6H_4Co(D_2H_2)$(2-mercaptoethanol), 78965-78-3; *p*-$FC_6H_4Co(D_2H_2)$(2-mercaptoethanol), 78965-79-4; *m*-$FC_6H_4Co(D_2H_2)CN^-$, 78965-80-7; *p*-$FC_6H_4Co(D_2H_2)CN^-$, 78965-81-8; *m*-$FC_6H_4Co(D_2H_2)SCN^-$, 78965-82-9; *p*-$FC_6H_4Co(D_2H_2)SCN^-$, 78965-83-0; *m*-$FC_6H_4Co(D_2H_2)NCS^-$, 78965-84-1; *p*-$FC_6H_4Co(D_2H_2)NCS^-$, 78965-85-2.

---

(33) Bromilow, J.; Brownlee, R. T. C.; Craik, D. J.; Sadek, M.; Taft, R. W. *J. Org. Chem.* **1980**, *45*, 2429–2438.

Contribution from the Department of Chemistry, La Trobe University,
Bundoora, Victoria, 3083, Australia

Applications of Molybdenum-95 Nuclear Magnetic Resonance Spectroscopy. 3.[1] Arenemolybdenum Tricarbonyl Derivatives

ANTHONY F. MASTERS,* ROBERT T. C. BROWNLEE, MAXWELL J. O'CONNOR,* and ANTHONY G. WEDD

Received December 31, 1980

The direct observation of the naturally abundant ^{95}Mo NMR spectra of $[LMo(CO)_3]$ (L = cycloheptatriene, mesitylene, *o*-, *m*-, and *p*-xylene, toluene, cyclopentadienyl anion) compounds are reported and discussed. Narrow resonances ($W_{h/2} \approx 6$ Hz) are observed, and the signals are the most shielded reported to date. The ^{95}Mo NMR chemical shift is related to the molybdenum–arene bond strength for L = arene. Arene exchange between $[LMo(CO)_3]$ derivatives is not detected at 38 °C in dichloromethane.

Introduction

We have recently demonstrated the potential of ^{95}Mo NMR spectroscopy in the study of molybdenum carbonyls.[2] Several important aspects emerged from our preliminary study. Thus, despite the quadrupole moment associated with this $I = {}^5/_2$ nucleus, line widths were often very narrow, allowing a combination of both sharp signals and rapid data accumulation and hence the possibility of routine detection of signals from dilute solutions. These benefits, coupled with the wide ^{95}Mo NMR chemical shift range observed to date (>4000 ppm)[2,3] have the further consequence that subtle electronic effects at

---

(1) For Part 2, see: Masters, A. F.; Gheller, S. F.; Brownlee, R. T. C.; O'Connor, M. J.; Wedd, A. G. *Inorg. Chem.* **1980**, *19*, 3866–3868.

(2) Masters, A. F.; Brownlee, R. T. C.; O'Connor, M. J.; Wedd, A. G.; Cotton, J. D. *J. Organomet. Chem.* **1980**, *195*, C17–C20.

(3) (a) Lutz, O.; Nolle, A.; Kroneck, P. *Z. Naturforsch.* **1976**, *31A*, 454–456. (b) Lutz, O.; Nolle, A.; Kroneck, P. *Ibid.* **1977**, *32A*, 505–506.

0020-1669/81/1320-4183$01.25/0 © 1981 American Chemical Society

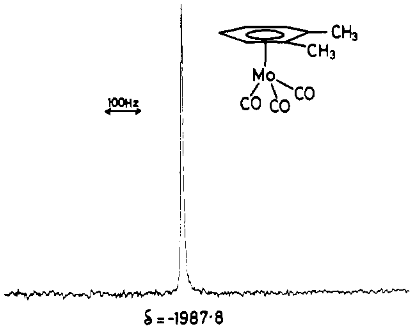

Figure 1. ^{95}Mo NMR spectrum of [(*o*-xyl)Mo(CO)$_3$], 0.5 M in CH$_2$Cl$_2$ at 22 °C. Spectral parameters: 1.1-s repetition time; 2000-Hz total spectral width: 4095 data points; 1000 transients.

the molybenum site and/or minor structural changes in the molybdenum environment can be readily resolved by ^{95}Mo NMR spectroscopy. This application of ^{95}Mo NMR data was illustrated by the sensitivity of the chemical shifts of (i) [Mo(CO)$_{6-n}$(P(OR$_3$)$_n$] (n = 1,3) to phosphite substituent and the value of n (these compounds, by virtue of molybdenum–phosphorus coupling, exhibit unequivocal "fingerprint" spectra), (ii) [(Cp)Mo(CO)$_3$R] to alkyl substituent variation some five bonds from the molybdenum center, and (iii) [(arene)-Mo(CO)$_3$] to arene substituents.

Since the majority of molybdenum compounds will yield only a single ^{95}Mo NMR resonance, a detailed understanding of the effects of ligand substituent variation on δ(^{95}Mo) is clearly fundamental to the wider application of ^{95}Mo NMR spectroscopy. We report here results for a series of [(arene)(Mo(CO)$_3$] compounds with the substituents located on a "π-bonded" aromatic ligand. A companion study of substituent effects in a series of [(Cp)Mo(CO)$_3$R] derivatives where the alkyl ligand is σ bonded to the metal has been completed.[4]

[(arene)Mo(CO)$_3$] derivatives are appropriate for study because of their many applications in organic synthesis and catalysis and their fundamental importance in organometallic chemistry.[5-10] Moreover, correlations with the NMR of other nuclei are possible since several complementary studies have been reported using ^{1}H, ^{13}C, ^{17}O, and ^{19}F NMR, albeit generally of the chromium analogues.[11-24]

Table I. ^{95}Mo NMR Parameters of [(arene)Mo(CO)$_3$] Derivatives in CH$_2$Cl$_2$

compd	temp, °C	δ(^{95}Mo)	$W_{h/2}$, Hz
[(cht)Mo(CO)$_3$]	22	−1684.0	13
Mo(CO)$_6$	22	−1856.7	4
[(mes)Mo(CO)$_3$]	22	−1906.9	8
	38	−1903.4	
[(*m*-xyl)Mo(CO)$_3$]	22	−1970.6	7
	38	−1967.6	
[(*p*-xyl)Mo(CO)$_3$]	22	−1979.2	5
	38	−1976.2	
[(*o*-xyl)Mo(CO)$_3$]	22	−1987.8	9
	38	−1985.0	
[(tol)Mo(CO)$_3$]	22	−2034.0	5
	38	−2031.7	
[(η^5-C$_5$H$_5$)Mo(CO)$_3$]$^-$	22	−2119.9^a	21
	22	−2122.8^b	18

^{a} As K$^+$ salt in DME. ^{b} As Na$^+$ salt in THF.

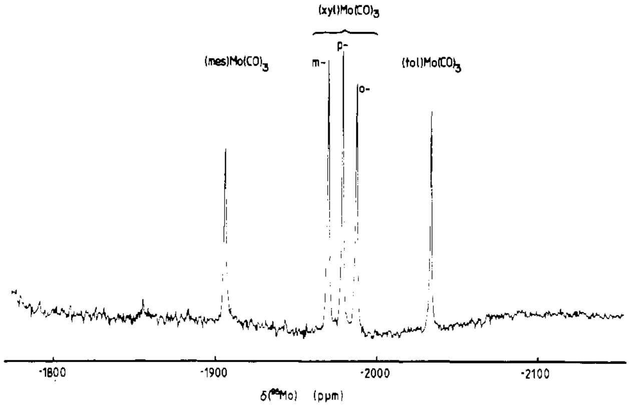

Figure 2. Room-temperature ^{95}Mo NMR spectrum of a mixture of [(arene)Mo(CO)$_3$] derivatives (arene = mes, *m*-, *p*-, and *o*-xyl, tol) in CH$_2$Cl$_2$, each approximately 0.2 M. Spectral parameters: 0.86-s repetition time, 2500-Hz total spectral width; 4095 data points; 5000 transients.

Experimental Section

All [(arene)Mo(CO)$_3$] compounds were synthesized by the method of Angelici,[25] viz., refluxing Mo(CO)$_6$ with the appropriate neat arene under nitrogen, and their identities confirmed by infrared spectroscopy.[26,27] (Cycloheptatriene)molybdenum tricarbonyl was prepared similarly.[28a] Salts of [(Cp)Mo(CO)$_3$]$^-$ were obtained via literature methods and were not isolated.[28b,29] All solvents and ligands were dried and manipulated under dry nitrogen by standard Schlenk and vacuum-manifold techniques. Samples for ^{95}Mo NMR spectra were sealed under vacuum shortly before use. Abbreviations used are the following: Cp = cyclopentadienyl anion (η^5-C$_5$H$_5^-$), cht = cycloheptatriene, tol = toluene, xyl = xylene, mes = mesitylene, benz = benzene, DME = dimethoxyethane, THF = tetrahydrofuran.

Spectra were obtained from naturally abundant samples with a JEOL PFT-100 NMR spectrometer (using a specifically tuned probe) operating in the pulsed Fourier transform mode at 6.5 MHz. Samples were measured at 22 °C unless otherwise stated, and signals are conventionally referenced to external aqueous 2 M Na$_2$MoO$_4$ at pH 11.[2] Digital resolution was 0.1 ppm (0.97 Hz) per data point. Concentrations were approximately 0.5 M. Typically a signal to noise ratio of 120 was obtained within 1000 transients (Figure 1).

---

(4) Masters, A. F.; Brownlee, R. T. C.; O'Connor, M. J.; Wedd, A. G.; Cotton, J. D.; Kimlin, H., to be submitted for publication.
(5) Semmelhack, M. F., *Ann. N.Y. Acad. Sci.* **1977**, *295*, 36–51.
(6) Jaouen, G. *Ann. N.Y. Acad. Sci.* **1977**, *295*, 59–78.
(7) Silverthorn, W. E. *Adv. Organomet. Chem.* **1975** *13*, 47–137.
(8) Korda, A.; Giezynski, R.; Krycinski, S. *J. Mol. Catal.* **1980**, *9*, 51–58.
(9) Saillard, J. Y.; Grandjean, D.; Choplin, F.; Kaufman, G. *J. Mol. Struct.* **1974**, *23*, 363–375.
(10) Farona, M. F. *Organomet. React. Synth.* **1977**, *6*, 223–288.
(11) McFarlane, W.; Grim, S. O. *J. Organomet. Chem.* **1966** *5*, 147–154.
(12) Fritz, H. P.; Kreiter C. G. *J. Organomet. Chem.* **1967**, *7*, 427–440.
(13) Emanuel, R. V.; Randall, E. W. *J. Chem. Soc. A* **1969**, 3002–3006.
(14) Farnell, L. F.; Randall, E. W.; Rosenberg, E. *J. Chem. Soc. D* **1971**, 1078–1079.
(15) Mann, B. E. *J. Chem. Soc. D* **1971**, 976–977.
(16) Mann, B. E. *J. Chem. Soc., Dalton Trans.* **1973**, 2012–2015.
(17) Todd, L. J.; Wilkinson, J. R. *J. Organomet. Chem.* **1974**, *77*, 1–25.
(18) Bodner, G. M.; Todd, L. J. *Inorg. Chem.* **1974**, *13*, 360–363.
(19) Bodner, G. M.; Todd, L. J. *Inorg. Chem.* **1974**, *13*, 1335–1338.
(20) Jackson, W. R.; Pincombe, C. F.; Rae, I. D.; Thapebinkarn, S. *Aust. J. Chem.* **1975**, *28*, 1535–1539.
(21) Hickey, J. P.; Wilkinson, J. R.; Todd, L. J. *J. Organomet. Chem.* **1979**, *179*, 159–168.
(22) Fletcher, J. L.; McGlinchey, M. J. *Can. J. Chem.* **1975**, *53*, 1525–1529.
(23) Roques, B. P.; Segard, C.; Combrisson, S.; Wehrli, F., *J. Organomet. Chem.* **1974**, *73*, 327–330.
(24) Adcock, W.; Aldous, G. L., submitted for publication in *J. Org. Chem.*
(25) Angelici, R. J. "Synthesis and Technique in Inorganic Chemistry", 2nd ed.; Saunders: Philadelphia, 1977; pp 132–133.
(26) Zingales, F.; Chiesa, A.; Basolo, F. *J. Am. Chem. Soc.* **1966**, *88*, 2707–2710.
(27) Pidcock, A.; Smith, J. D.; Taylor, B. W. *J. Chem. Soc. A* **1967**, 872–876.
(28) King, R. B. "Organometallic Synthesis" Academic Press: New York, 1965; Vol. 1: (a) pp 126–127; (b) pp 156–151.
(29) Jolly, W. L. *Inorg. Synth.* **1968**, *11*, 116–118.

Results and Discussion

The ^{95}Mo NMR spectral details are collected in the Table I, while Figure 1 illustrates a typical spectrum, that of [(*o*-xyl)Mo(CO)$_3$]. The spectra are characterized by narrow line widths and are the most shielded signals observed to date. Lutz[30] has concluded from a combination of ^{95}Mo and ^{97}Mo NMR data that the quadrupole interaction represents an essential relaxation mechanism for $[MoO_nS_{4-n}]^{2-}$ (n = 0–4) species, and this can reasonably be expected to be significant in the present case. The narrow line widths of the table are probably a consequence of a high local symmetry at the molybdenum (approximately C_{3v}, with the arene orientation considered to be averaged). In an analogous series of manganese derivatives, the asymmetry parameter has been shown by ^{55}Mn nuclear quadrupole resonance to be very small.[31] It may be significant that [(cht)M(CO)$_3$] has both an apparently higher barrier to hydrocarbon rotation[20,32] and the broadest ^{95}Mo NMR signal. We have observed the very considerable effects of solvent changes on the ^{95}Mo NMR chemical shift and line width in the [(Cp)Mo(CO)$_3$R] system.[4] However, in the present study, the anion [(Cp)Mo(CO)$_3$]$^-$ has approximately the same chemical shift and line width with different cations and in different solvents.

A single comparison between ^{95}Mo and ^{13}C NMR illustrates the anticipated lower sensitivity of the latter to changes at the molybdenum. While the π-arene ligand has the same effect on carbonyl ^{13}C shielding as do three monodentate R_3P ligands,[17] $\delta(^{95}Mo)$ for [(mes)Mo(CO)$_3$] is about 200 ppm upfield of that for *fac*-[Mo(CO)$_3$(P(OEt)$_3$)$_3$].[2]

Figure 2 demonstrates how easily ^{95}Mo NMR spectroscopy can discriminate between the mesitylene, xylene, and toluene derivatives in an approximately equimolar mixture. In particular, the resonances of the three xylenes are clearly separated, and identification of the signal from each isomer is trivial by comparison with the complexity expected in the corresponding ^{1}H or ^{13}C NMR spectra. Assignments have been made by comparison with the spectra of the pure samples, and the peaks of the mixture show no variations in chemical shift or line widths relative to those of individual species. Essentially the same spectrum is obtained at 38 °C in CH_2Cl_2. Thus, although [(arene)M(CO)$_3$] compounds exchange with added arene at elevated temperatures.[33-36] and with ligands such as phosphines at ambient temperature,[26,27,37] there is no exchange of arenes between these molybdenum derivatives on the ^{95}Mo NMR time scale under the present conditions. It seems unlikely, therefore, that arene substitution under these conditions involves complete prior dissociation of the arene as has been variously discussed.[10,34,35] Indeed, even at 80 °C in tetrachloroethane there is no ^{95}Mo NMR evidence for exchange of [*o*-xyl)Mo(CO)$_3$] with either [(mes)Mo(CO)$_3$] or mesitylene. The simplicity of the ^{95}Mo NMR spectrum obviously lends itself admirably to studies of such exchange and substitution processes (e.g., both the [(arene)Mo(CO)$_3$] and [(PR$_3$)$_3$Mo(CO)$_3$] ^{95}Mo NMR signals can be observed during substitution at room temperature), and we are currently pursuing these possibilities.

Two trends in chemical shift are apparent from Table I: (i) the chemical shift of this class of compounds and (ii) the ordering of $\delta(^{95}Mo)$ within the class. The present series of compounds exhibits highly shielded ^{95}Mo NMR signals, the only other compound significantly shielded with respect to Mo(CO)$_6$ being the hydride, [HMo$_2$(CO)$_{10}$]$^-$.[38] Large negative chemical shifts can, in general, be associated with low formal oxidation states,[39] and, in this respect, [(arene)Mo(CO]$_3$] compounds *as a class* have ^{95}Mo NMR chemical shifts compatible with zerovalent molybdenum. In particular, the species [(Cp)Mo(CO)$_3$]$^-$ and [HMo$_2$(CO)$_{10}$]$^-$ have net negative charges, formally zerovalent molybdenums, and large negative values of $\delta(^{95}Mo)$. Other workers[13,18] have interpreted a shielding of arene ^{1}H and ^{13}C NMR resonances on complexation of M(CO)$_3$ as being consistent with a net withdrawal of electron density from the arene ring by the M(CO)$_3$ units, as suggested by other physical and chemical studies.[6,18,40] The electron-withdrawing role of the M(CO)$_3$ fragment is then consistent with the highly shielded ^{95}Mo NMR signals of the [(arene)Mo(CO)$_3$] species *as a class*.

While the concept of high electron density on molybdenum satisfactorily accounts for the high shielding of this *class* of compounds, increasing methyl substitution on the arene results in a progressive deshielding of the ^{95}Mo nuclei *within* the class: ^{95}Mo nuclear shielding decreases in the order tol > *o*-xyl > *p*-xyl > *m*-xyl > mes (Table I). That is, increasing the ring methyl substitution, which is expected to increase the electron density in the aryl ring and presumably also around the Mo nucleus, leads in fact to a shift in $\delta(^{95}Mo)$ to *low* field.

There have been attempts to understand chemical shifts for quadrupolar nuclei in terms of the Ramsey equation.[41] These attempts have met with limited success due to the complexity of the calculations. Other workers have attempted to rationalize anomalous carbonyl ^{13}C and ^{17}O chemical shifts in [(arene)Cr(CO)$_3$] derivatives in terms of the effect of distant ring substituents on metal–carbonyl π bonding.[19,21] It appears premature to attempt a detailed explanation of the trend in the ^{95}Mo chemical shift detailed in Table I. However, correlations with experimental observables will guide future theoretical studies and an interesting correlation does exist. The rate of substitution[42] of arene by a given nucleophile, e.g., P(OMe)$_3$, in [(arene)Mo(CO)$_3$] + 3P(OMe)$_3$ → *cis*-[Mo(CO)$_3$(P(OMe)$_3$)$_3$] + arene decreases in the order *o*-xyl > tol > *p*-xyl > *m*-xyl > mes. This order is essentially the same as the former chemical shift order. Thus the rate of arene substitution decreases with increasing methyl ring substitution, an effect attributed to a progressive strengthening of the metal–arene bond.[27] Independent thermodynamic data exists[43-46] which confirms an increase in molybdenum–arene bond strength with increasing ring methyl substitution in these compounds.

It therefore appears that decreased ^{95}Mo nuclear shielding is consistent with molybdenum–arene bond strength. However,

---

(30) Kroneck, P.; Lutz, O.; Nolle, A. *Z. Naturforsch.* **1980**, *35A*, 226–229.

(31) Brill, T. B.; Kotlar, A. J. *Inorg. Chem.* **1974**, *13*, 470–474.

(32) Kreiter, C. G.; Larg, M.; Strack, H. *Chem. Ber.* **1975**, *108*, 1502–1510.

(33) Strohmeier, W.; Mittnacht, H. *Chem. Ber.* **1960**, *93*, 2085–2086.

(34) Strohmeier, W.; Mueller, R. *Z. Phys. Chem.* (*Wiesbaden*) **1964**, *40*, 85–95.

(35) Mahaffy, C. A. L.; Pauson, P. L. *J. Chem. Res. Synop.* **1979**, 126–127; *J. Chem. Res., Miniprint* **1979**, 1752–1755.

(36) Mahaffy, C. A. L.; Pauson, P. L. *J. Chem. Res., Synop.* **1979**, 128; *J. Chem. Res. Miniprint* **1979**, 1776–1794.

(37) Pidcock, A.; Taylor, B. W. *J. Chem. Soc. A* **1967**, 877–879.

(38) Masters, A. F.; Brownlee, R. T. C.; O'Connor, M. J.; Wedd, A. G., unpublished results: δ −1937 (^{95}Mo NMR), J(Mo–H) = 15 Hz, $W_{h/2}$ = 34 Hz.

(39) Heaton, B. T.; Brown, C.; Smith, D. O.; Strona, L.; Goodfellow, R. J.; Chini, P.; Martinengo, S. *J. Am. Chem. Soc.* **1980**, *102*, 6175–6177.

(40) Sennikov, P. G.; Kuznetsov, V. A.; Egorochkin, A. N.; Sirotkin, N. I.; Nazarova, R. G.; Razuvaev, G. A. *J. Organomet. Chem.* **1980**, *190*, 167–176.

(41) (a) Webb, G. A. In "NMR and the Periodic Table"; Harris, R. K., Mann, B. E., Eds.; Academic Press: London, 1978. (b) Kidd, R. G., *Annu. Rep. NMR Spectrosc.* **1980**, *10*, 1–79.

(42) The kinetic data have been obtained in both methylcyclohexane and 1,2-dichloroethane at 50 °C and an S_N2 mechanism has been proposed.[26,27,37]

(43) Adedeji, F. A.; Brown, D. L. S.; Connor, J. A.; Leung, M. L.; Paz-Andrade, I. M.; Skinner, H. A. *J. Organomet. Chem.* **1975**, *97*, 221–228.

(44) Connor, J. A.; Martinho-Simoes, J. A.; Skinner, H. A.; Zafarani-Moattar, M. T. *J. Organomet. Chem.* **1979**, *179*, 331–356.

(45) Brown, D. L. S.; Connor, J. A.; Demain, C. P.; Leung, M. L.; Martinho-Simoes, J. A.; Skinner, H. A.; Zafarani-Moattar, M. T. *J. Organomet. Chem.* **1977**, *142*, 321–335.

(46) Skinner, H. A. *J. Chem. Thermodyn.* **1978**, *10*, 309–320.

a quantitative interpretation is clearly not yet possible because of the present incomplete understanding of the complexity and relative importance of the several terms in the Ramsey equation. Interestingly, decreased ^{17}O nuclear shielding has been correlated[47-49] with increased Mo=O π-bond strength, an effect which was related to the angular momentum term in the Ramsey equation.[49]

Summary

The [(arene)$Mo(CO)_3$] derivatives give high-quality ^{95}Mo NMR spectra characterized by significant molybdenum shielding and well-separated narrow signals. Resolution of signals due to the various arenes and ready discrimination between isomers are thus possible. Considerable spectral simplification relative to ^1H and ^{13}C NMR is obvious, and there is no evidence for arene exchange below 38 °C. The foregoing illustrates the complementary information available with the use of ^{95}Mo, ^{13}C, ^{17}O, and ^1H NMR, and in fact with the present study, all nuclei of the (arene)$Mo(CO)_3$ molecules have been probed by NMR spectroscopy.

In the present [(arene)$Mo(CO)_3$] system, there are two effects which determine the observed ^{95}Mo chemical shift. First, and most importantly, the well-established charge donation from the arene to molybdenum results in these arene derivatives, *as a class*, having shielded molybdenum nuclei (with respect to those of other classes such as carbonyl phosphites,[2] carbonyl alkyls,[4] molybdates,[1] etc.). Second, more subtle bonding effects around molybdenum causes ordering of $\delta(^{95}Mo)$ *within* this class of compounds. In particular there is an interesting correlation between the ^{95}Mo nuclear shielding and Mo–arene bond strength.

It is important to note, however, that inversion in substituent chemical shifts and bond order/chemical shift relationships are known.[50-52] The ^{95}Mo chemical shifts of less than 50 compounds have so far been reported, and further development of the ^{95}Mo NMR chemical shift scale and an adequate theory of chemical shifts in quadrupolar nuclei must precede a more complete understanding of the ^{95}Mo chemical shift.

Acknowledgment. We thank the Australian Wool Corporation and the Australian Research Grants Committee for financial support and Dr. B. T. Heaton for communicating results prior to publication.

Registry No. (cht)$Mo(CO)_3$, 12125-77-8; (mes)$Mo(CO)_3$, 12089-15-5; (*m*-xyl)$Mo(CO)_3$, 12288-65-2; (*p*-xyl)$Mo(CO)_3$, 12093-13-9; (*o*-xyl)$Mo(CO)_3$, 12288-64-1; (tol)$Mo(CO)_3$, 12083-34-0; $K[(\eta^5\text{-}C_5H_5)Mo(CO)_3]$, 62866-01-7; $Na[(\eta^5\text{-}C_5H_5)Mo(CO)_3]$, 12107-35-6; $Mo(CO)_6$, 13939-06-5.

---

(47) Miller, K. F.; Wentworth, R. A. D. *Inorg. Chem.* **1979**, *18*, 984–988.

(48) Filowitz, M.; Ho, R. K. C.; Klemperer, W. G.; Shum, W. *Inorg. Chem.* **1979**, *18*, 93–103.

(49) Kidd, R. G. *Can. J. Chem.* **1967**, *45*, 605–608.

(50) Bromilow, J.; Brownlee, R. T. C.; Page, A. V. *Tetrahedron Lett.* **1976**, 3055–3058.

(51) Adcock, W.; Abeywickrema, A. N. *Tetrahedron Lett.* **1979**, 1809–1810.

(52) Miller, K. F.; Wentworth, R. A. D. *Inorg. Chem.* **1980**, *19*, 1818–1821.

Contribution from the Department of Chemistry and Biochemistry,
James Cook University of North Queensland, Queensland 4811, Australia

Dynamic ^1H Nuclear Magnetic Resonance Line-Broadening Study of Adduct Formation between Azidocobalt(III) Complexes Containing Organic Ligands and Lanthanide Shift Reagent

LEONARD F. LINDOY* and HON WAY LOUIE

Received May 15, 1981

The interaction of Eu(fod-d_9)$_3$ with a series of cobalt(III) complexes [of which (pyridine)azido[*N,N'*-ethylenebis(acetylacetoniminato)]cobalt(III) is the parent complex] in $CDCl_3$ has been investigated by using ^1H (and ^{13}C) NMR. The addition of Eu(fod-d_9)$_3$ results in induced shifts in the spectra of the respective cobalt complexes, and 1:1 adduct formation has been shown to occur in each case. Certain proton signals were found to broaden initially and then narrow as Eu(fod-d_9)$_3$ was incrementally added. Maximum broadening occurred when the Eu(fod-d_9)$_3$:cobalt complex ratio was between 0.3 and 0.4. From the concentration dependence of the chemical shifts, together with the observed line widths, the lifetimes of the adducts have been calculated; lifetimes of 10^{-3}–10^{-4} s were obtained. The study provides new examples of the nondilute case of fast-exchange line broadening—a case little studied in the past.

Introduction

Since their introduction in 1969,[1] lanthanide shift reagents (LSRs) have been routinely used to simplify the NMR spectra of organic compounds containing suitable heteroatoms.[2,3] To a lesser extent these reagents have also been employed in NMR studies of organometallic compounds,[3,4] but only isolated examples of their use for similar studies involving coordination complexes have appeared.[5-7] For example, LSRs have been employed to distinguish between N-bonded and S-bonded thiocyanato ligands[5] in suitable metal complexes as binding of the LSR only occurs to the uncoordinated nitrogen atom when the thiocyanate is S bonded. When the thiocyanate is N bonded, no interaction occurs. As in the above example, most of the studies with organometallic complexes have involved interaction of the LSR at heteroatom sites other than the donor atoms of the particular ligand present. Nevertheless, in previous papers[8-11] we have described studies in which co-

---

(1) Hinkley, C. C. *J. Am. Chem. Soc.* **1969**, *91*, 5160–5162.

(2) Sanders, J. K. M.; Williams, D. H. *Nature* (*London*) **1972**, *240*, 385–390. Mayo, B. C. *Chem. Soc. Rev.* **1973**, *2*, 49–74. Reuben, J. *Prog. Nucl. Magn. Reson. Spectrosc.* **1973**, *9*, 3–69. Cockerill, A. F.; Davies, G. L.; Harden, R. C.; Rackham, D. M. *Chem. Rev.* **1973**, *73*, 553–588.

(3) Sievers, R. E., Ed. "Nuclear Magnetic Resonance Shift Reagents"; Academic Press: New York, 1973.

(4) See for example: Foreman, M. I.; Leppard, D. G. *J. Organomet. Chem.* **1971**, *31*, C31–C33. Gielen, M.; Goffin, N.; Topart, J. *Ibid*, **1971**, *32*, C38–C40. Paul, J.; Schloegl, K ; Silhan, W. *Monatsh. Chem.* **1972**, *103*, 243–254. Johnson, B. F. G.; Lewis, J.; McArdle, P.; Norton, J. R. *J. Chem. Soc., Dalton Trans.* **1974**, 1253–1258. Reger, D. L. *Inorg. Chem.* **1975**, *14*, 660–664. Dickson, R. S.; Johnson, S. H.; Rae, I. D. *Aust. J. Chem.* **1975**, *28*, 1681–1687.

(5) Anderson, S. J.; Norbury, A. H. *J. Chem. Soc., Chem. Commun.* **1975**, 48–49.

(6) Tauszik, G. R.; Pellizer, G.; Costa, G. *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 717–721. Nonoyama, M.; Sato, K.; Yamagski, K. *Nippon Kagaku Kaishi* **1974**, 695–702.

(7) Hendrickson, A. R.; Hope, J. M.; Martin, R. L. *J. Chem. Soc., Dalton Trans.* **1976**, 2032–2039.

(8) Lindoy, L. F.; Moody, W. E. *J. Am. Chem. Soc.* **1977**, *99*, 5863–5870.

0020-1669/81/1320-4186$01.25/0