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Molybdenum-95 nuclear magnetic resonance studies on molybdenum carbonyl complexes of isonitriles and amines

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Abstract

The ^{95}Mo NMR spectra of 28 molybdenum carbonyl complexes of isonitriles and amines are reported. Within similar classes of complexes excellent correlation is found between ^{95}Mo chemical shifts and ligand π-acceptor ability and, more importantly, complex structures. Application to the analysis of diastereomeric complexes is reported. From analysis of linewidths and relaxation behavior, the surprising result is found that ^{95}Mo linewidths in isonitrile complexes are not due to coupling to the electric field gradient, but to scalar coupling between the ^{95}Mo and ^{14}N nuclei which, in turn, is inversely proportional to the substitution number n in complexes $Mo(CO)_{6-n}(CNR)_n$. A dependence of chemical shift on temperature of 0.3 ppm/°C is found for $Mo(CO)_6$.

Introduction

In the last decade, molybdenum-95 nuclear magnetic resonance has been shown to be a useful analytical method for characterizing complexes of molybdenum [1,2]. In particular, the demonstration of the potential of ^{95}Mo NMR for the study of organometallic systems in 1980 has led to rapid progress [3]. This is in spite of the only 15.7% natural abundance and the presence of an electric quadrupole moment ($I = 5/2$). Early studies were confined to compounds with relatively symmetric ligand fields with zero or small electric field gradients and, thus, narrow linewidths. Studies have since demonstrated that much useful information can be obtained even from compounds of low symmetry. The relative sensitivity of ^{95}Mo NMR, along with the moderate-to-short spin–lattice relaxation times of the ^{95}Mo nucleus in typical complexes, make it quite possible to obtain useful spectra, often with considerably less acquisition time than would be required for other means of analysis, for example ^{13}C NMR.

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All oxidation states of molybdenum from +6 to 0 have been examined by ^{95}Mo NMR and the resultant chemical shift range spans 7000 ppm. Molybdenum(0) carbonyl complexes occur in the shielded range (−700 to −2200 ppm) relative to the reference standard Na_2MoO_4 (2 *M* in D_2O at pH 11). Three trends emerge from examination of the literature data on molybdenum(0) carbonyl complexes to date. First, there is good agreement between the ordering of chemical shifts in $Mo(CO)_5L$ and Horrocks' [4] π-bonding spectrochemical series. Thus, the ^{95}Mo chemical shift for $Mo(CO)_5L$ indicates deshielding with decreasing π-acceptor ability in the series $CO > P(OR)_3 > PR_3 > NR_3$. Second, for a given ligand L, there is a clear deshielding progression of chemical shifts with increasing *n* in $Mo(CO)_{6-n}L_n$. For example, the ^{95}Mo chemical shifts for the complexes $Mo(CO)_5[P(OMe)_3]$, $Mo(CO)_4[P(OMe)_3]_2$, $Mo(CO)_3[P(OMe)_3]_3$, $Mo(CO)_2[P(OMe)_3]_4$, $Mo(CO)[P(OMe)_3]_5$, $Mo[P(OMe)_3]_6$ are −1864, −1827, −1756, −1660, −1518, and −1358 ppm, respectively [5]. Third, assignment of structure for new phosphine or phosphite complexes based on ^{95}Mo chemical shifts is difficult due to the fact that small changes in structure induce large changes in chemical shift. For example, the data just cited would not allow one to correctly assign the resonance of −1762 ppm to the complex $Mo(CO)_4[P(O\text{-}^iPr)_3]_2$ [6].

Among the many possible molybdenum(0) complexes, compounds containing isonitrile ligands have not previously been investigated by ^{95}Mo NMR [7,8]. We report here on such an investigation, discussing both chemical shift and the relaxation behavior and linewidth of several complexes. Unlike molybdenum complexes containing phosphine and phosphite ligands, those containing isonitrile ligands show excellent correlations between structures and chemical shifts. We also discuss results for a number of complexes with nitrogen-based ligands, which, like the isonitrile complexes, are of chemical interest as potential catalysts for allylic alkylation reactions [9].

Results and discussion

Chemical shifts

The results of the molybdenum-95 NMR spectroscopic studies on isonitrile complexes presented in Table 1 provide some interesting results. First, between groups of complexes having the same substitution number, there is a clear demarcation in chemical shifts. In contrast, there are only small chemical shift differences between complexes of methyl, butyl, tert-butyl, benzyl, phenyl, and 2,6-dimethylphenyl isonitrile. This contrasts sharply with the results discussed above for complexes containing phosphine or phosphite ligands where small changes in ligand electronics and structure, most likely manifested by changes in cone angle [10], induce large chemical shift changes. Thus, unlike the phosphine and phosphite complexes, isonitrile complexes appear to be amenable to structural characterization by ^{95}Mo NMR.

Second, the similarity in π-acceptor ability between isonitrile ligands and the carbonyl ligand can be seen in the relatively small changes in chemical shifts occuring upon increasing ligand substitution in the series $Mo(CO)_{6-n}(CNR)_n$. The approximately 140 ppm chemical shift difference between $Mo(CO)_6$ and $Mo(CO)_2(CNR)_4$ is rather small when considering the normal range of ^{95}Mo NMR chemical shifts.

Table 1

^{95}Mo NMR data for molybdenum isonitrile complexes

Entry	Complex	Number	Chemical shift (ppm) [a]	$\Delta\nu_{1/2}$ (Hz)
1	$Mo(CO)_6$	**1**	−1858	0.14
2	$Mo(CO)_5(CNMe)$	**2**	−1850	5.8
3	$Mo(CO)_5(CN^tBu)$	**3**	−1849	6.8
4	*cis*-$Mo(CO)_4(CNMe)_2$	**4**	−1829	4.2
5	*cis*-$Mo(CO)_4(CN^tBu)_2$	**5**	−1825	7.0
6	*fac*-$Mo(CO)_3(CNBn)_3$	**6**	−1792	3.8
7	*fac*-$Mo(CO)_3(CNBu)_3$	**7**	−1791	4.1
8	*fac*-$Mo(CO)_3(CNMe)_3$	**8**	−1786	4.4
9	*fac*-$Mo(CO)_3(CN^tBu)_3$	**9**	−1782	8.0
10	*fac*-$Mo(CO)_3(CN\text{-}2,6\text{-}Me_2Ph)_3$	**10**	−1783	1.6
11	*fac*-$Mo(CO)_3(CNPh)_3$	**11**	−1772	[b]
12	*cis*-$Mo(CO)_2(CNBu)_4$	**12**	−1731	4.3
13	*cis*-$Mo(CO)_2(CN^tBu)_4$	**13**	−1714	6.2
14	*cis*-$Mo(CO)_2(CN\text{-}2,6\text{-}Me_2Ph)_4$	**14**	−1711	5.2
15	*cis*-$Mo(CO)_2(CNPh)_4$	**15**	−1699	4.5

[a] All spectra were recorded in dichloromethane solvent unless noted otherwise. [b] This complex was detected as an impurity in $Mo(CO)_2(CNPh)_4$; linewidth could not be determined.

Third, the relative order of chemical shifts for alkyl and aryl isonitrile complexes is surprising. Based on evidence from other workers on the spectroscopic and chemical properties of isonitrile complexes [11] and our own experimental results on the use of isonitrile complexes as allylic alkylation catalysts [9], aryl isonitriles are generally considered to be better π-acceptor ligands than alkyl isonitriles. Yet, in the ^{95}Mo NMR spectra, the aryl isonitrile complexes occur deshielded relative to the corresponding alkyl isonitrile complexes, indicating a poorer π-accepting ability. A rationale for this discrepancy is not immediately evident, but paramagnetic contributions to the chemical shift may be involved [12].

Fourth, it is rather remarkable that all of the isonitrile complexes have linewidths less than 10 Hz. While $Mo(CO)_6$, MoL_6 and, surprisingly, $Mo(CO)_3L_3$ complexes are expected to have narrow linewidths due to the absence of an electric field gradient [13,14*], $Mo(CO)_4L_2$ and $Mo(CO)_2L_4$ complexes typically have linewidths of 20–200 Hz. The narrow linewidths in the isonitrile complexes must reflect the good π-acceptor ability and high symmetry, and thus similarity to CO, of the isonitrile ligands. These two factors will serve to maintain smaller electric field gradients, and hence narrower NMR linewidths, in isonitrile complexes. Further discussion of the linewidths is given below.

The ^{95}Mo NMR chemical shifts for a number of complexes with nitrogen-based ligands have also been investigated and the results are presented in Table 2. The results are particularly interesting with regard to structural and electronic characterization. NMR of transition metal nuclei has been reported to be a more sensitive probe than optical spectroscopy for locating ligands in the spectrochemical series [15]. The relative order of chemical shifts in Table 2 is in accord with the expected π-acceptor ability of the various ligands [16]. Thus, decrease in π-accep-

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* Reference number with asterisk indicates a note in the list of references.

Table 2

^{95}Mo NMR data for molybdenum amine complexes

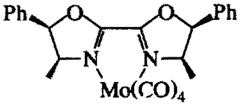
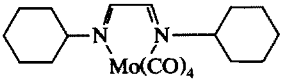
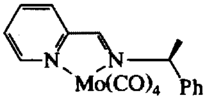
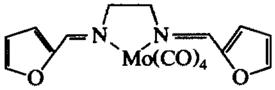
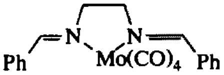
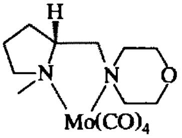
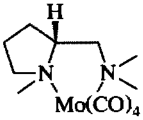
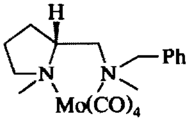
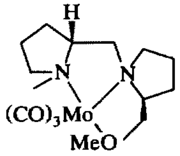
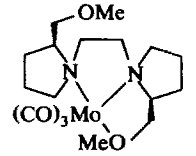
Entry	Complex	Number	Chemical shift (ppm) [a]	$\Delta\nu_{1/2}$ (Hz)
1	$Mo(CO)_6$	**1**	−1858	0.14
2	$Mo(CO)_6$	**1**	−1855 [b]	≤ 0.1
3		**16**	−1256	130
4		**16**	−1284 *b*	120
5		**17**	−1209	57
6		**17**	−1240 [b]	37
7		**18**	−1181	64
8		**18**	−1206 [b]	45
9	$Mo(CO)_4$bpy	**19**	−1165	90
10	 1 : 3 mixture *trans,trans : trans,cis*	**20**	−1165, −1170	60, 150
11		**21**	−1153	61
12		**22**	−1024	100
13	$Mo(CO)_4$TMEDA	**23**	−1010	56
14		**24**	−1004	56
15		**25**	−987	150
16		**26**	−808	83

Table 2 (continued)

Entry	Complex	Number	Chemical shift (ppm) [a]	$\Delta\nu_{1/2}$ (Hz)
17	 4 : 1 mixture of isomers	**27**	−806, −833	65, 75
18	$Mo(CO)_3(pyr)_3$	**28**	−800 [c]	7

[a] All spectra were recorded in dichloromethane solvent unless noted otherwise. [b] Acetonitrile-d_3 solvent was employed. [c] Pyridine solvent [18].

tor ability in the series isonitrile > bis(2-oxazoline) > diimine > diamine corresponds to high frequency shifts in the ^{95}Mo NMR spectra. Beyond this gross trend, fine changes in electronic structure are also revealed in the data. Increasingly deshielded chemical shifts in entries 5–11 confirm the decrease in π-acceptor ability in the series: conjugated diimine > 2-pyridyl imine > 2,2′-bipyridyl > nonconjugated diimine. However, the comparison between the chemical shifts of complexes **26** and **27** with the value reported for complex **28** is quite surprising. The differences in donor and acceptor properties between an ether unit and a pyridine would be expected to exert a greater change in the ^{95}Mo NMR chemical shift. A rationale for the observed chemical shifts is not apparent.

In addition to detection of electronic perturbations, ^{95}Mo NMR can be a sensitive probe for stereochemistry. In particular, it can be a probe for diastereomeric complexes [17]. Based on ^{1}H NMR data, the diimine complex in Entry 10 was suspected to be a 3 : 1 mixture of isomers. This proposal is supported by the observation of two signals in the ^{95}Mo NMR spectrum. The symmetric minor isomer with a trans, trans ligand is shown, while the major isomer containing a cis, trans ligand is not. The symmetry of the minor isomer is also supported by the narrower linewidth of its NMR signal. The diastereomeric complexes of Entry 15 (2 : 1 by ^{1}H NMR) were not resolved, and only a broad signal was observed. The deshielded chemical shifts for the complexes in Entries 16 and 17 confirm the tridentate coordination of the ligand suggested by the IR data. Additionally, the ^{95}Mo NMR spectrum of the complex of Entry 16 supports the ^{1}H NMR observation of a single diastereomeric complex. The two diastereomeric complexes of Entry 17 (only one shown) were not detected in the relatively complicated proton spectrum, but were readily observed in the ^{95}Mo NMR spectrum.

The ^{95}Mo NMR chemical shifts are only modestly affected by changes in solvent. While the chemical shift changes seen in Entries 1–8 may seem numerically significant, taken as a percentage of the chemical shift, they are all less than 3%. These solvent induced shifts are significantly less than what is typically observed in ^{1}H NMR [19].

It should be noted that advances have been recently made in theoretical predictions of chemical shift values [20]. Combariza *et al.* have used *ab initio* LORG (Localized Orbital–Local Origins) methods to calculate isotropic and tensor shielding data. However, the basis sets employed do not allow accurate predictions of the subtle variations in chemical shifts observed for molybdenum(0) complexes. Additionally, compounds of the complexity reported herein are, unfortunately, beyond the realm of *ab initio* methods.

Relaxation and linewidths

Molybdenum-95 has a substantial electric quadrupole moment (0.12×10^{-24} cm^2), which should lead to a large nuclear quadrupole coupling constant in cases where an electric field gradient exists at the Mo nucleus. Thus, any complex with such a gradient should have a fairly wide line in its ^{95}Mo NMR spectrum as a result of efficient nuclear relaxation via the quadrupole interaction. By and large, this is what is seen for complexes for which ^{95}Mo NMR results have been reported [1].

A notable exception to the generally wide lines seen in ^{95}Mo NMR is the spectrum of $Mo(CO)_6$. Being an octahedrally symmetric complex, there is no electric field gradient at molybdenum, thereby suppressing the quadrupolar relaxation mechanism. Also as a result of the symmetry, the chemical shift anisotropy is zero, thus removing this as a possible relaxation mechanism. The spin–lattice relaxation time (for ^{95}Mo) of this complex has been reported as ~ 7 s at ambient temperature [21], a remarkably long T_1 for a quadrupolar nucleus, but fully consistent with the lack of any effective relaxation mechanism.

Contrasting sharply with this long T_1 are the reported linewidths for the molybdenum nucleus in $Mo(CO)_6$ [1], which range from approximately to 1 to 10 Hz. It would be expected that under the usual conditions of measurement (ambient temperature, low viscosity solvents) the linewidth should be in the order of $(\pi T_1)^{-1}$, and therefore 1–2 orders of magnitude smaller than values so far reported. It occurred to us that molybdenum chemical shifts, like those of many transition metals, might be quite sensitive to temperature. The observed linewidths would then be determined largely by thermal gradients across the sample, as Allerhand has shown to be the case for ^{13}C linewidths [22]. By carefully controlling temperature and thermal gradients across the sample (using apparatus and methods described by Allerhand for ultra-high resolution ^{13}C NMR), we observed a ^{95}Mo linewidth in the order of 0.1 Hz for $Mo(CO)_6$, approaching the intrinsic linewidth expected on the basis of the measured T_1. Measurements of chemical shift as a function of temperature gave coefficients of 0.29 ppm/°C (6.8 Hz/°C at 23.45 MHz) in dichloromethane and 0.31 ppm/°C (7.2 Hz/°C at 23.45 MHz) in acetonitrile for this complex [23]. Thus, temperature effects may have contributed to the sizeable linewidths reported for $Mo(CO)_6$. In addition, while few if any other complexes are likely to have lines as narrow as that for $Mo(CO)_6$, careful temperature control is still important for accurate chemical shift determinations.

Though an order of magnitude or more greater than for the $Mo(CO)_6$ line, the linewidths for all the isonitrile complexes examined were both substantially less than the linewidths more often observed for molybdenum complexes, and quite uniform. The relatively narrow linewidths are easily understood as a result of the considerable chemical similarity of CO and isonitriles as ligands, resulting in much smaller electric field gradients in isonitrile complexes than are found in complexes containing other ligands. On the other hand, the constancy of the linewidths was somewhat surprising. Given the substantial electric quadrupole moment of the ^{95}Mo nucleus, one would expect the relaxation times to be very sensitive to even

Table 3

Relaxation times and linewidths

Complex	T_1 (s)	T_2 (s)	$\Delta\nu_{1/2}$ (T_1 calc.) (Hz)	$\Delta\nu_{1/2}$ (observed) (Hz)
$Mo(CO)_5(CNMe)$ (**2**)	0.68	0.49	0.47	5.8
$Mo(CO)_4(CNMe)_2$ (**4**)	1.08	0.35	0.29	4.2
$Mo(CO)_3(CNMe)_3$ (**8**)	0.77	0.19	0.41	4.4

small differences between the various complexes, and the linewidths likewise to show more variability.

To see what factors might be at work in these complexes, the spin–lattice relaxation times (T_1) were measured for the series $Mo(CO)_{6-n}(CNMe)_n$ for $n = 1$–3 (**2**, **4**, **8**, respectively), and Carr–Purcell–Meiboom–Gill experiments (CPMG) were performed in an attempt to measure transverse relaxation times (T_2) [24]. The results are given in Table 3, from which it can be seen that while spin-lattice relaxation times show no apparent trend, the "spin–spin relaxation times" show a clear, regular progression. Also apparent is a large discrepancy between linewidths expected ($[\pi T]^{-1}$) from either T_1 or T_2 and observed linewidths.

For the irregular variation in T_1's there is no apparent easy explanation. If one assumes the relaxation is due entirely to the quadrupole mechanism, then the different relaxation rates simply indicate small electronic differences among the various complexes. Since the symmetry of the isonitrile complexes is lowered (from O_h), the chemical shift tensors for ^{95}Mo are now anisotropic, leading to the possibility that this might also be contributing to the relaxation. Relaxation time measurements at several field strengths would serve to confirm and quantify this hypothesis, as would comparison of the ^{95}Mo to the ^{97}Mo relaxation times.

Having seen that the observed linewidths were essentially unrelated to T_1 for the isonitrile complexes, we next undertook transverse relaxation time measurements, using CPMG. It quickly became apparent that meaningful data were impossible to obtain; results for any complex depended entirely upon the interval between successive refocussing pulses of which they should, in principle, be independent [24,25*]. In particular, a longer delay between successive 180° pulses resulted in a shorter observed transverse relaxation time. This, however, provides the confirmation for a hypothesis that in the isonitrile complexes, the linewidth is due to unresolved scalar coupling between the ^{95}Mo and ^{14}N nuclei. The decrease in T_2 for ^{95}Mo with a longer interval between successive refocussing pulses simply reflects the greater likelihood of a ^{14}N spin flip, leading to less complete refocussing of the ^{95}Mo transverse magnetization. It should be noted that ^1J (^{95}Mo–^{14}N) values in nitrosyl complexes have been reported to be of the order of 45 Hz [26].

Even this does not adequately explain the constancy of the ^{95}Mo linewidths, however. If they are in fact due to unresolved scalar coupling to nitrogen, one might expect that the ^{95}Mo linewidth should increase with an increasing number of isonitrile ligands present, contrary to observation. In order to have a constant linewidth, it would also be necessary for the spin–lattice relaxation time of the nitrogen to shorten on going from **2** to **8**. The shorter the T_1 for nitrogen, the more complete the "self-decoupling", and the sharper the ^{95}Mo line, balancing the broadening expected for an increased number of ligands.

That this is the case can be deduced from the proton spectra of the free ligand and the three complexes. It is known that the nitrogen in an isonitrile has an unusually long T_1; in CH_3NC it is several seconds, allowing the ^{14}N–^{1}H coupling of 2.2 Hz to be easily resolved [27]. The proton spectrum of CH_3NC is a 1:1:1 triplet, each line being approximately 0.6 Hz wide at half-height. In the series **2**–**4**–**8**, the methyl protons all appear as broad singlets, that for **2** being broadest (2 Hz) and that for **8** the sharpest (1.3 Hz). This is due entirely to the shortening of the nitrogen T_1, and is precisely the same concept considered above for ^{95}Mo. The reason for this shortening of T_1 for ^{14}N is, of course, the increasing distortion of the electronic structure of the isonitrile, as compared to the free ligand, as the amount of π-backbonding to the isonitrile ligand increases with increasing substitution number. Such distortion can be manifested by bending of the nitrogen substituent away from linearity which has been documented by X-ray structure determinations of isonitrile complexes [28]. However, it is notable that ^{95}Mo NMR can be such a sensitive probe for this electronic distortion since structural nonlinearity is only clearly evident in homoleptic isonitrile complexes. The overall effect of increasing substitution by isonitriles is, therefore, formation of an electric field gradient about the ^{14}N nucleus which results in a shortened T_1 and decreased coupling to ^{1}H and ^{95}Mo nuclei.

The amine complexes we observed had linewidths of 50–200 Hz, another 1 to 2 orders of magnitude greater than for the isonitrile complexes, and much more typical of ^{95}Mo linewidths. Having seen that 2-bond coupling of molybdenum to nitrogen is non-negligible, we were curious as to whether the linewidths of the amine complexes might also be due in part to scalar coupling to the coordinated nitrogen. As a test case, we chose the complex $Mo(CO)_4$ TMEDA (**23**), in which nitrogen is in a relatively symmetric environment and therefore has the greatest likelihood of showing a scalar coupling to molybdenum. The linewidth (^{95}Mo) for this complex is 60 Hz; the T_1 we measured was 5.5 ms, corresponding to a calculated linewidth ($[\pi T_1]^{-1}$) of 58 Hz. Thus, for the amine complexes it would appear that the linewidth in the ^{95}Mo spectrum is due entirely to the efficient quadrupolar relaxation of the molybdenum.

Conclusions

We have demonstrated application of ^{95}Mo NMR to structural and electronic analysis of molybdenum(0) complexes containing isonitrile and nitrogen-based ligands. Unlike the more studied phosphine complexes, the systems reported here, including diastereomeric complexes, were quite amenable to structural characterization by ^{95}Mo NMR. Unusual scalar coupling, which is inversely proportional to substitution number, has been documented for molybdenum carbonyl complexes containing methyl isonitrile ligands.

Experimental

All reactions were carried out under a positive pressure of dry nitrogen in flame dried glassware. Solvents were distilled before use: benzene, diethyl ether, tetrahydrofuran (THF) and toluene from sodium benzophenone ketyl; acetonitrile and dichloromethane from calcium hydride; pyridine and triethylamine from potassium hydroxide. Molybdenum hexacarbonyl was used as received as a gift from Pressure Chemical Company. Proton nuclear magnetic resonance spectra were recorded on Bruker WP-200 (200 MHz), WP-270 (270 MHz) or AM-500 (500 MHz) spectrometers. Carbon-13 nuclear magnetic resonance spectra were obtained on JEOL FX-60 (15 MHz), JEOL FX-200 (50 MHz) or Bruker AM-500 (125 MHz) spectrometers. Infrared spectra were recorded in 0.1 mm path length sodium chloride cavity cells on Beckman acculab 7, Perkin–Elmer 1420, or Mattson Polaris spectrometers. Mass spectra were recorded on AE1-MS902, Kratos MS25 or Kratos MS80 instruments at an ionizing voltage of 70 eV unless otherwise noted. Microanalyses were performed by Spang Microanalytical Laboratories, Eagle Harbor, Michigan.

All ^{95}Mo NMR spectra were recorded on a Bruker AM-360, operating at 23.45 MHz. All spectra were taken at 300 K, with active temperature control, and with broadband proton decoupling (WALTZ-16, using IW). All complexes which were soluble in dichloromethane were dissolved in this solvent, with 10% d_6-benzene added for locking purposes. Others were taken as solutions in acetonitrile-d_3. Acquisition times were typically twice the inverse of the expected linewidth, using a pulse angle of approximately 30° and no delay between scans. Peak positions are reported with respect to an external standard of Na_2MoO_4 in D_2O ($pH > 11$) and are corrected for the difference in chemical shift between D_2O and the lock solvent used for each complex. Spin–lattice relaxation times were determined by the inversion-recovery method [29], using a composite 180° pulse [30]. The data were treated using a 3-parameter fit (to I_0, I_{00} and T_1), using standard Bruker software for the analysis. Spin–spin relaxation times were measured with the Carr–Purcell–Meiboorn–Gill sequence [24], also using the 3-parameter fit supplied with Bruker software for treating the experimental data. Linewidths were generally determined as the best fit Lorentzian line, again using standard Bruker software. Particularly noisy spectra (those with the broadest lines) did not always give reliable results because of low signal-to-noise ratio, and for these the linewidth was estimated simply as the frequency separation between points at half-maximum on the peak. In no case was any window multiplication of the FID done before Fourier transformation.

All complexes were prepared via ligand exchange starting with molybdenum hexacarbonyl. Compounds were prepared as described previously: compounds **2**, **3**, **5**, and **9** from ref. [31]; compounds **4**, **6**, **7**, **8**, **10**, **12**, **13**, **14**, **15**, **17**, **20**, and **21** from ref. [9]; compound **19** from ref. [32] and compound **23** from ref. [33]. Proline derived ligands were used as obtained from Professor T. Mukaiyama.

*(4*R*,4'*R*,5*S*,5'*S*)-4,4'-Dimethyl-5,5'-diphenyl-2,2'-bis(2-oxazoline)*

A solution of diethyl oxalimidate (1.44 g, 10.0 mmol) and norephedrine hydrochloride (3.80 g, 20.2 mmol) in ethanol (30 ml) was stirred at room temperature for 40 h. It was added to chloroform (100 ml) and the chloroform solution was washed with dilute aqueous sodium bicarbonate (100 ml), water (100 ml), saturated aqueous sodium chloride (100 ml) and dried ($MgSO_4$). The solvent was removed *in vacuo* and the crude material was purified by flash chromatography (99:1 chloroform/methanol) and recrystallization (90:10 hexane/chloroform) to yield 2.03 g

(63%) of white needles; m.p. 135–37°C. $[\alpha]_{589}^{24}$ +457.7 (c 1.27, $CHCl_3$). IR ($CHCl_3$): 2990, 1620, 1490, 1450, 1220, 1140, 950 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 0.92 (6H, d, $J = 7.1$ Hz), 4.70 (2H, dq, $J = 10.0$, 7.1 Hz), 5.83 (2H, d, $J = 10.0$ Hz), 7.25–7.45 (10H, m). Anal. Found: C, 74.96; H, 6.26. $C_{20}H_{20}N_2O_2$ calc.: C, 74.98; H, 6.29%. MS: 320 (M^+, 2), 203 (11), 160 (39), 144 (14), 142 (13), 132 (11), 118 (100), 91 (14). Mass Found: 320.1523. $C_{20}H_{20}N_2O_2$ calc.: 320.1525.

*[(4*R*,4'*R*,5*S*,5'*S*)-4,4'-Dimethyl-5,5'-diphenyl-2,2'-bis(2-oxazoline)]tetracarbonylmolybdenum (16)*

A solution of hexacarbonylmolybdenum (0.370 g, 1.4 mmol) and (4*R*,4*R'*,5*S*, 5'*S*)-4,4'dimethyl-5,5'-diphenyl-2,2'-bis(2-oxazoline) (0.448 g, 1.4 mmol) in toluene (3 ml) was refluxed for 1.5 h. It was concentrated to about 1 ml, hexane was added (5 ml) and the solution was cooled to 0°C. The precipitate was filtered, washed with hexane and dried *in vacuo* to yield 0.719 g (97%) of a dark red solid. IR ($CHCl_3$): 2015, 1905, 1885, 1840, 1470, 1220, 980, 940 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 1.08 (6H, d, $J = 7.1$ Hz), 4.75 (2H, dq, $J = 10.1$, 7.1 Hz), 6.21 (2H, d, $J = 10.1$ Hz), 7.20–7.30 (4H, m), 7.31–7.45 (6H, m). ^{95}Mo NMR (23.45 HMz, CH_2Cl_2): δ −1256 ($\Delta\nu_{1/2} = 130$ Hz). ^{95}Mo NMR (23.45 HMz, CH_3CN): δ −1284 ($\Delta\nu_{1/2} = 120$ Hz).

N-*(2'-Pyridinyl)methylene-(*S*)-1-phenylethylamine*

To a solution of pyridine-2-carboxaldehyde (0.884 g, 8.25 mmol) and anhydrous sodium sulfate (0.50 g, 3.52 mmol) in ether (5 ml) was added (*S*)-(−)-(1)-phenylethylamine. The solution was stirred at room temperature for 24 h and then filtered through magnesium sulfate. The solvent was removed *in vacuo* and the product was kugelrohr distilled (110°C, 0.5 mm) to yield 1.700 g (98%) of a pale yellow oil. IR ($CHCl_3$): 3060, 2980, 2930, 2870, 1715, 1650, 1590, 1570, 1495, 1470, 1450, 1435, 1370, 1080, 990, 905, 700 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 1.62 (3H, d, $J = 6.8$ Hz), 4.62 (1H, $J = 6.8$ Hz), 7.20–7.50 (6H, m), 7.71 (1H, t, $J = 7.6$ Hz), 8.09 (1H, d, $J = 7.6$ Hz), 8.48 (1H, s), 8.63 (1H, d, $J = 4.4$ Hz). Anal. Found: C, 79.94; H, 6.76. $C_{14}H_{14}N_2$ calc.: C, 79.97; H: 6.71. $[\alpha]_{589}^{23}$ + 38.5 (c 1.50, $CHCl_3$).

*[*N*-(2'-Pyridinyl)methylene-(*S*)-1-phenylethylamine]tetracarbonylmolybdenum (18)*

A solution of hexacarbonylmolybdenum (0.600 g, 2.27 mmol) and *N*-(2'-pyridinyl)methylene-(*S*)-1-phenylethylamine (0.478 g, 2.27 mmol) in toluene (7 ml) was refluxed for 1.5 h. After cooling, the solution was concentrated to 2 ml and hexane (8 ml) was slowly added. The precipitate was filtered, washed with hexane (2 × 3 ml) and dried *in vacuo* to yield 0.864 g (91%) of a red powder. IR ($CHCl_3$): 3020, 2980, 2010, 1915, 1890, 1835, 1600, 1465 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 1.95 (3H, d, $J = 6.8$ Hz), 5.30 (1H, q, $J = 6.8$ Hz), 7.25–7.48 (6H, m), 7.75 (1H, d, $J = 7.6$ Hz), 7.90 (1H, m), 8.58 (1H, s), 9.09 (1H, d, $J = 5.5$ Hz). Anal. Found: C, 51.44; H, 3.32; N, 6.74. $C_{18}H_{14}MoN_2O_4$ calc.: C, 51.69; H, 3.37; N, 6.70%. MS: 422 (4, M^+), 420 (14, M^+), 419 (6, M^+), 418 (10, M^+), 417 (8, M^+), 416 (4, M^+), 414 (8, M^+), 392 (1), 364 (2), 336 (24), 308 (69), 281 (15), 210 (15), 195 (67), 105 (100), 104 (43). Mass Found: 420.0010. $C_{18}H_{14}{}^{98}MoN_2O_4$ calc.: 420.0005. ^{95}Mo NMR (23.45 MHz, CH_2Cl_2): δ −1181 ($\Delta\nu_{1/2} = 64$ Hz). ^{95}Mo NMR (23.45 MHz, CH_3CN): δ −1206 ($\Delta\nu_{1/2} = 45$ Hz).

[(S-1-Methyl-2-[(morpholin-1-yl)methyl]pyrrolidine]tetracarbonylmolybdenum (22)

A solution of hexacarbonylmolybdenum (0.400 g, 1.515 mmol) and (*S*)-1-methyl-2-[(morpholin-1′-yl)methyl)pyrrolidine (0.279 g, 1.515 mmol) in toluene (4 ml) was refluxed for 2 h. The yellow solution was cooled to room temperature and the resulting crystals were filtered, washed with hexane (2 × 1 ml) and dried *in vacuo* to yield 0.568 g (96%) of light yellow needles. IR ($CHCl_3$): 2005, 1890, 1875, 1830 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.45–1.65 (1H, m), 1.75–2.50 (5H, m), 2.54–2.70 (1H, m), 2.79 (3H, s), 2.85–3.00 (2H, m), 3.22–3.56 (4H, m), 3.80–4.00 (2H, m), 4.12–4.43 (2H, m). LD/FTMS: Mass Found: 405.0077. $C_{13}H_{20}K^{98}MoN_2O_4$ calc.: 405.0114. ^{95}Mo NMR (23.45 MHz, CH_2Cl_2): δ −1024 ($\Delta\nu_{1/2} = 100$ Hz).

[(S-1-Methyl-2-(dimethylaminomethyl)pyrrolidine]tetracarbonylmolybdenum (24)

A solution of hexacarbonylmolybdenum (0.400 g, 1.515 mmol) and (*S*)-1-methyl-2-(dimethylaminomethyl)pyrrolidine (0.2155 g, 1.515 mmol) in toluene (2.5 ml) was refluxed for 105 min. The yellow solution was concentrated to 1 ml and stored at 0°C overnight. The resulting crystals were filtered, washed with hexane (2 × 1 ml) and dried *in vacuo* to yield 0.4594 g (87%) of yellow prisms. IR ($CHCl_3$): 2015, 1895, 1830, 1465, 910 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.40–1.60 (1H, m), 1.80–2.25 (4H, m), 2.29 (1H, dd, $J = 13$, 3.7 Hz), 2.78 (2H, m), 2.79 (3H, s), 2.80 (3H, s), 2.84 (3H, s), 3.27–3.55 (3H, m). ^{95}Mo NMR (23.45 MHz, CH_2Cl_2): δ −1004 ($\Delta\nu_{1/2} = 56$ Hz).

[(S)-1-Methyl-2-(benzylmethylaminomethyl)pyrrolidine]tetracarbonylmolybdenum (25)

A solution of hexacarbonylmolybdenum (0.264 g, 1.00 mmol) and (*S*)-1-methyl-2-(benzylmethylaminomethyl)pyrrolidine (0.2183 g, 1.00 mmol) in toluene (2 ml) was refluxed for 2 h. The yellow solution was concentrated to 1 ml; 1 ml of hexane was added and the solution was stored at 0°C overnight. The resulting crystals were filtered, washed with hexane (2 × 1 ml) and dried *in vacuo* to yield 0.350 g (82%) of yellow crystals. IR ($CHCl_3$): 2010, 1890, 1870, 1830 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) 2:1 diastereomeric mixture: δ 1.41–1.58 (1H, m), 1.80–2.62 (5H, m), 2.69 (1H, s), 2.77 (2H, s), 2.80 (2H, s), 2.89 (1H, s), 3.30–3.75 (3H, m), 4.72 (0.7H, d, $J = 14$ Hz), 4.28 (0.3H, d, $J = 14$ Hz), 4.41 (0.7H, d, $J = 14$ Hz), 4.55 (0.3H, d, $J = 14$ Hz), 7.14–7.45 (5H, m). ^{95}Mo NMR (23.45 MHz, CH_2Cl_2): δ −987 ($\Delta\nu_{1/2} = 150$ Hz). Anal. Found: C, 50.70; H, 5.37; N, 6.45. $C_{18}H_{22}MoN_2O_4$ calc.: C, 50.71; H, 5.20; N, 6.57.

[(2S,2′S)-2-Methoxymethyl-1-[(1′-methylpyrrolidin-2′-yl)methyl]pyrrolidine]tricarbonylmolybdenum (26)

A solution of hexacarbonylmolybdenum (0.300 g, 1.136 mmol) and (2*S*,2′*S*)-2-methoxymethyl-1-[(1′-methylpyrrolidin-2′-yl)methyl]pyrrolidine (0.2412 g, 1.136 mmol) in toluene (2 ml) was refluxed for 105 min. The yellow solution was cooled at 0°C overnight. The resulting crystals were filtered, washed with hexane (2 × 1 ml) and dried *in vacuo* to yield 0.3200 g (67%) of yellow needles. IR ($CHCl_3$): 2980, 1915, 1780, 1760, 1450, 1055, 930 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.32–1.60 (2H, m), 1.70–2.24 (6H, m), 2.52 (1H, m), 2.53 (3H, s), 2.70–3.40 (6H, m), 3.58–4.00 (3H, m), 3.84 (3H, s). MS: 394 (0.50, M^+), 392 (0.28, M^+), 391 (0.27,

M^+), 388 (0.24, M^+), 336 (0.47), 306 (0.46), 236 (1), 149 (1), 128 (11), 97 (11), 84 (100), 69 (15), 57 (13). Mass Found: 392.0784. $C_{15}H_{24}{}^{96}MoN_2O_4$ calc.: 392.0776. Anal. Found: C, 45.84; H, 6.09; N, 6.95. $C_{15}H_{24}MoN_2O_4$ calc.: C, 45.93; H, 6.17; N, 7.14. ^{95}Mo NMR (23.45 MHz, CH_2Cl_2): δ −808 ($\Delta\nu_{1/2} = 83$ Hz).

1,2-Bis[(2'S)-2'-methoxymethylpyrrolidinyl]ethane

A solution of (2*S*)-2-methoxymethylpyrrolidine (1.00 g, 8.68 mmol), triethylamine (3 ml, 21.5 mmol) and 1,2-dibromoethane (0.8155 g, 4.34 mmol) in benzene (15 ml) was refluxed for 7 h. The mixture was added to chloroform (50 ml) and washed with 10% aqueous potassium hydroxide solution (30 ml) and saturated aqueous sodium chloride solution (30 ml). The chloroform solution was dried ($MgSO_4$) and the solvents were removed *in vacuo*. The crude material was distilled (88–90°C, 0.01 mm) to yield 0.7590 (68%) of the product as a colorless oil. $[\alpha]^{24}_{589}$ −131.9 (c, 1.0, $CHCl_3$). IR ($CHCl_3$): 2920, 1460, 1110, 910 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.60–1.68 (2H, m), 1.68–1.82 (4H, m), 1.84–1.92 (2H, m), 2.19 (2H, td, $J = 9.1, 7.7$ Hz), 2.37–2.45 (2H, m), 2.52–2.58 (2H, m), 2.98–3.07 (2H, m), 3.14 (2H, ddd, $J = 9.2, 7.0, 2.5$ Hz), 3.30 (2H, dd, $J = 9.4, 6.2$ Hz), 3.35 (6H, s), 3.41 (2H, dd, $J = 9.4, 4.5$ Hz). MS: 257 (0.28, $M + 1^+$), 224 (3), 211 (3), 193 (4), 179 (4), 142 (12), 128 (100), 96 (14), 83 (15), 44 (47). Mass Found: 257.2227. $C_{14}H_{29}N_2O_2$ ($M + 1$) calc.: 257.2222.

[1,2-Bis{(2'S)-2'-methoxymethylpyrrolidinyl}ethane]tricarbonylmolybdenum (27)

A solution of hexacarbonylmolybdenum (0.264 g, 1 mmol) and 1,2-bis[2'*S*)-2-methoxymethylpyrrolidinyl]ethane (0.2564 g, 1 mmol) in toluene (2.5 ml) was refluxed for 2 h. The solution was cooled to 80°C, hexane (1 ml) was added, and then it was cooled to room temperature. The solvent was removed from the resulting crystals, which were then washed with hexane (2 × 1 ml) and dried *in vacuo* to yield 0.2677 g (58%) of yellow needles. IR ($CHCl_3$): 2960, 2920, 1910, 1775, 1755, 1455 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.50–2.10 (6H, m), 2.13–2.45 (2H, m), 2.45–2.87 (4H, m), 2.89–3.21 (3H, m), 3.21–3.55 (7H, m), 3.55–3.89 (5H, m), 3.89–4.05 (1H, m). ^{95}Mo NMR (23.45 MHz, CH_2Cl_2) (4:1 diastereomeric mixture): δ −806 ($\Delta\nu_{1/2} = 65$ Hz), 833 ($\Delta\nu_{1/2} = 75$ Hz).

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