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Registry No. **1**, 86992-66-7; **2**, 86943-70-6; **3**, 86943-72-8; **4**, 86943-73-9; **5**, 86943-74-0; **6**, 86943-76-2; [Rh(nbd)(PNP)]PF$_6$, 86953-28-8; [Ir(cod)(PNP)]BF$_4$, 86953-30-2; [Ir(cod)Cl]$_2$, 12112-67-3.

Supplementary Material Available: Tables of general temperature factor expressions, calculated hydrogen atom positional parameters, and calculated and observed structure factor amplitudes for **1** and **2**, figures of ^{31}P NMR spectra for compounds **2**, **3**, **4**, and **6**, and stereoviews of **1** and **2** (62 pages). Ordering information is given on any current masthead page.

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Chemical, Spectral, and Structural Features of $\mathrm{Mo(RC{\equiv}CR)_2(S_2CNC_4H_4)_2}$ Complexes Containing the Electronically Unique Pyrrole-*N*-carbodithioate Ligand

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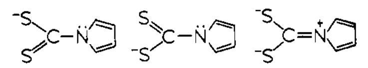
Syntheses of a series of bis(alkyne)bis(pyrrole-*N*-carbodithioato)molybdenum(II) complexes, including the unsubstituted acetylene derivative $\mathrm{Mo(HC_2H)_2(S_2CNC_4H_4)_2}$, are reported. The molecular structure of the 2-butyne adduct, $\mathrm{Mo(MeC_2Me)_2(S_2CNC_4H_4)_2}$, has been determined by a single-crystal X-ray diffraction study. The crystals were found to be monoclinic of space group $P2_1/n$ with $a = 12.372$ (4) Å, $b = 12.145$ (3) Å, $c = 14.184$ (3) Å, and $\beta = 101.50$ (2)°. The unit cell contains one independent molecule per asymmetric unit; the structure was refined to $R = 0.056$ and $R_w = 0.041$ with use of 1470 reflections with $I > 3\sigma(I)$. The molecular geometry can be described as a distorted octahedron with two cis-parallel alkynes and two bidentate carbodithioates in the coordination sphere. The pyrrole-*N*-carbodithioate ligands are essentially planar with a C–N distance of 1.37 Å (average) in the $\mathrm{S_2C{-}NC_4H_4}$ unit. The ring distances within the $\mathrm{NC_4H_4}$ moiety are compared to those of free pyrrole and cyclopentadiene to address the question of aromaticity in this fragment. Dynamic NMR studies revealed two independent fluxional processes in $\mathrm{Mo(MeC_2Me)_2(S_2CNC_4H_4)_2}$. The lower energy process ($\Delta G^* = 10.7$ kcal/mol) is believed to reflect rotation around the C–N bond of the chelating ligands while the higher energy molecular rearrangement (13.7 kcal/mol) is believed to correspond to rotation of the alkyne ligands around the molybdenum–alkyne bond axis. Both the crystallographic and DNMR results reflect the pyrrole nitrogen's reluctance to provide π-electron density to the $\mathrm{CS_2}$ fragment. The decreased electron donor ability of the pyrrole-*N*-carbodithioate ligand relative to that of alkyl analogues is chemically evident in the lability of the carbonyl ligand in $\mathrm{Mo(CO)(RC_2R)(S_2CNC_4H_4)_2}$, which greatly enhances the rate of formation of the bis(alkyne) products. The chemical, spectroscopic, and structural properties of these complexes can be rationalized in terms of accepted valence bond descriptions of carbodithioate ligands.

Introduction

The chemistry of low-oxidation-state, formally electron-deficient d^4 transition-metal monomers containing both π-acid and π-base ligands has matured substantially.[1] A useful model of the electronic structure of these compounds[2] has been distilled from the spectroscopic,[3-6] structural,[1,7,8] theoretical,[9] electrochemical[1c,10] and mechanistic[11] results accumulated for these complexes.

A significant subclass of six-coordinate d^4 monomers is the set of bis(dithiocarbamato) derivatives of the type $\mathrm{M(X)(Y)(S_2CNR_2)_2}$ (M = Mo, W; X = Y = CO;[12] X = CO, Y = $\mathrm{R^1C_2R^2}$;[7,13] X = O, Y = $\mathrm{R^1C_2R^2}$;[4,8,14] X = Y = $\mathrm{R^1C_2R^2}$[2,3,6]). The dithiocarbamate ligands serve to anchor these complexes by providing a variable degree of π-electron donation as evident in the chemistry[12] and structure[15] of $\mathrm{Mo(CO)_2(S_2CNR_2)_2}$. Contributions from the three resonance forms (I–III) which



I II III

dominate metal–dithiocarbamate valence bond descriptions are relatively insensitive to minor variations of alkyl and aryl substituents on the nitrogen atom.[16] The pyrrole-*N*-carbodithioate ligand (pdtc) prepared by Kellner et al.[17] exhibits unusual bonding properties in homoleptic dithiocarbamate complexes. Bereman and his co-workers have substantiated the hypothesis that resonance form III is unfavorable for pdtc

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ligands due to loss of pyrrole aromaticity upon delocalization of the nitrogen lone pair into the CS_2 unit.[18]

We initiated a study of bis(alkyne)bis(pyrrole-*N*-carbodithioato)molybdenum(II) monomers in an effort to systematically modify the molecular properties of these complexes relative to those of the previously reported $Mo(R^1C_2R^2)_2(S_2CNR_2)_2$ (R = Me, Et) complexes. We report here (1) the remarkably facile synthesis and the spectroscopic characterization of $Mo(R^1C_2R^2)_2(pdtc)_2$ complexes (pdtc = $^-S_2CNC_4H_4$; $R^1 = R^2 = Ph$; $R^1 = Ph$, $R^2 = H$, $R^1 = Ph$, $R^2 = Me$, $R^1 = R^2 = Me$, $R^1 = R^2 = Et$; $R^1 = n\text{-Bu}$, $R^2 = H$; $R^1 = R^2 = H$), (2) the successful synthesis of the parent bis(acetylene) complex, (3) the solid-state molecular structure of $Mo(MeC_2Me)_2(pdtc)_2$ illustrating the cis-parallel alkyne orientation, and (4) DNMR studies reflecting a decreased $S_2C{=}N$ π-interaction in the pyrrole-*N*-carbodithioate ligand compared to that in dialkyldithiocarbamate analogues.

Experimental Section

Materials and Methods. Standard Schlenk techniques with a dry deoxygenated nitrogen atmosphere were used for all manipulations. Solvents were degassed prior to use. Molybdenum hexacarbonyl, pyrrole, carbon disulfide, iodine, chlorine gas, tetraethylammonium iodide, and alkynes were obtained from commerical sources. Acetone was removed from acetylene gas by bubbling the gas through a saturated sodium metabisulfite/water solution followed by passing through a calcium chloride drying tube. $Mo(CO)_3(S_2CNC_4H_4)_2$,[19] $Mo(CO)_4Cl_2$,[20] $KS_2CNC_4H_4\cdot{}^1/_2THF$,[18] and $[(C_2H_5)_4N][Mo(CO)_5I]$[21] were prepared according to literature procedures. Proton NMR (100 MHz) spectra were recorded on a Varian XL-100 spectrometer. Carbon-13 NMR (62.89 MHz) spectra were recorded on a Bruker WM 250 spectrometer. Chemical shifts are reported as parts per million downfield of Me_4Si. NMR sample temperatures were measured with a thermocouple located in the probe. A Beckman IR 4250 spectrometer was used to record infrared spectra, which were calibrated with a polystyrene standard.

Syntheses. $Mo(R^1C_2R^2)_2(S_2CNC_4H_4)_2$. (a) From $Mo(CO)_3(S_2CNC_4H_4)_2$ ($R^1 = R^2 = Ph$; $R^1 = Ph$, $R^2 = H$; $R^1 = Ph$, $R^2 = Me$; $R^1 = R^2 = Me$; $R^1 = R^2 = Et$; $R^1 = n\text{-Bu}$, $R^2 = H$). The following preparative procedure is general for the synthesis of the alkyne complexes listed above. $Mo(CO)_3(S_2CNC_4H_4)_2$ (1.08 g, 2.33 mmol) was dissolved in ether (30 mL), producing a purple solution (substitution of tetrahydrofuran for ether also leads to a purple solution while methylene chloride produces an orange solution; all are suitable solvents for the reaction). PhC_2Ph (0.822 g, 4.61 mmol) was added to the solution while it was stirring. The solution immediately turned brown, and gas evolved. The solution IR shows a strong carbonyl band at 1955 cm^{-1} at this point which disappears with time. After 4 h solvent was removed in vacuo. The oily brown product was chromatographed on an alumina column with a methylene chloride/toluene solvent mixture. The optimum solvent ratio varies depending on the alkyne substituents with more soluble alkylalkynes requiring more toluene. An orange band was eluted, and decomposition products remained on the column. The solution volume was reduced, methanol was added, and the flask was placed in a refrigerator. The solid that precipitated was filtered, washed with methanol, and dried in vacuo to yield moderately air-stable orange crystals in 30–40% yield. Isolation of $Mo(n\text{-}BuC_2H)_2(S_2CNC_4H_4)_2$ varied from this scheme because it produced an oil despite recrystallization attempts with various solvents.

(b) From $[(C_2H_5)_4N][Mo(CO)_5I]$ ($R^1 = R^2 = Ph$; $R^1 = Ph$, $R^2 = H$; $R^1 = Ph$, $R^2 = Me$; $R^1 = R^2 = Me$; $R^1 = R^2 = Et$). The following preparative procedure is general for the synthesis of the alkyne complexes listed above. $[(C_2H_5)_4N][Mo(CO)_5I]$ (0.75 g, 1.52 mmol) was dissolved in tetrahydrofuran (25 mL), forming a yellow solution. Iodine (0.386 g, 1.52 mmol) was added, immediately producing an orange-red solution. After 15 min the iodine had been completely consumed. The hygroscopic pyrrole-*N*-carbodithioate ligand, $K[S_2CNC_4H_4]\cdot{}^1/_2THF$ (0.660 g, 3.04 mmol), which had been previously transferred into a tared Schlenk tube, was added by connecting the neck joints of the two Schlenk flasks and inverting to drop the ligand into the solution. The solution immediately turned dark red, and gas evolved. After the mixture was stirred for 15 min, dimethylacetylene (0.23 mL, 0.16 g, 0.304 mmol) was added. The solution began to turn brown and displayed a strong CO stretch at 1953 cm^{-1} in the IR spectrum. After 4 h solvent was removed in vacuo. The product was chromatographed and recrystallized as described above to yield large orange crystals (53% yield).

$Mo(PhC_2Ph)_2(S_2CNC_4H_4)_2$: ^1H NMR ($CDCl_3$) δ 7.59 (m, 4 H, α-H), 7.36 (m, 20 H, C_6H_5), 6.29 (m, 4 H, β-H).

$Mo(PhC_2H)_2(S_2CNC_4H_4)_2$: ^1H NMR ($CDCl_3$) δ 10.66 (s, 2 H, $H{-}C{\equiv}$), 7.62 (m, 4 H, α-H), 7.39 (m, 10 H, C_6H_5), 6.30 (m, 4 H, β-H).

$Mo(PhC_2Me)_2(S_2CNC_4H_4)_2$: ^1H NMR ($CDCl_3$) δ 7.67 (m, 4 H, α-H), 7.45 (m, 10 H, C_6H_5), 6.32 (m, 4 H, β-H), 3.11 (s, 6 H, CH_3).

$Mo(MeC_2Me)_2(S_2CNC_4H_4)_2$: ^1H NMR ($CDCl_3$) δ 7.64 (m, 4 H, α-H), 6.25 (m, 4 H, β-H), 2.65 (s, 12 H, CH_3); ^{13}C NMR (C_7D_8) δ 215.94 (s, S_2C), 179.53 and 178.76 (s, ${\equiv}C$), 118.09 (d, α-C), 114.24 (d, β-C).

$Mo(EtC_2Et)_2(S_2CNC_4H_4)_2$: ^1H NMR ($CDCl_3$) 7.67 (m, 4 H, α-H), 6.28 (m, 4 H, β-H), 2.79–3.47 (poor q, 8 H, CH_2), 1.16 (t, 12 H, CH_3); IR (KBr) $\nu(C{\equiv}C)$ 1787 (w) cm^{-1}.

$Mo(n\text{-}BuC_2H)_2(S_2CNC_4H_4)_2$: ^1H NMR ($CDCl_3$) δ 9.94 (s, 2 H, $H{-}C{\equiv}$), 7.69 (m, 4 H, α-H), 6.36 (m, 4 H, β-H), 3.16 (m, 4 H, ${\equiv}C{-}CH_2$), 1.03–1.81 (m, 8 H, ${\equiv}C{-}CH_2{-}CH_2{-}CH_2$), 0.88 (m, 6 H, CH_3). IR (KBr) $\nu(C{\equiv}C)$ 1715 (w) cm^{-1}.

$Mo(HC_2H)_2(S_2CNC_4H_4)_2$. $Mo(CO)_3(S_2CNC_4H_4)_2$ (1.52 g, 3.27 mmol) was dissolved in 50 mL of CH_2Cl_2. Acetylene gas, purified as described above, was bubbled through the methylene chloride solution. An infrared spectrum of the brown solution showed a strong carbonyl stretch at 1962 cm^{-1} after 10 min. After 1.5 h this band had disappeared. The acetylene gas flow was stopped, and solvent was removed on a rotary evaporator. The product was chromatographed on an alumina column with methylene chloride as eluent. A brown-orange band was eluted with most of the material remaining as decomposition product on the column. Solvent was removed in vacuo to yield an oily solid. The bis(acetylene) product was obtained in 10% yield by this method but contained minor impurities, which we were unable to separate from the product. ^1H NMR ($CDCl_3$) δ 10.28 (s, 4 H, $H{-}C{\equiv}$), 7.69 (m, 4 H, α-H), 6.30 (m, 4 H, β-H).

Collection of Diffraction Data. Orange crystals of $Mo(MeC_2Me)_2(S_2CNC_4H_4)_2$ were grown from a cooled solution of methylene chloride and methanol. A roughly rectangular prism having approximate dimensions 0.22 × 0.27 × 0.30 mm was selected, mounted on a glass wand, and coated with epoxy cement. Diffraction data were collected on an Enraf-Nonius CAD-4 automated diffractometer.[22] A monoclinic cell was indicated from 25 centered reflections found in the region $30° < 2\theta < 34°$ and refined by least-squares calculations. The cell parameters are listed in Table I.

Diffraction data were collected in the quadrant $+h,+k,\pm l$ under the conditions specified in Table I. Three standard reflections were monitored for decay every 5 h, and the crystal was recentered as necessary every 300 reflections. A total of 4056 data were processed and corrected for Lorentz–polarization effects. No correction was made for absorption. A total of 1470 data having $I > 3\sigma(I)$ were used in the refinement of the structure.

Solution and Refinement of the Structure. The structure solution was straightforward from application of the heavy-atom method. The space group $P2_1/n$ deduced from systematic absences ($h0l$ ($h + l = 2n + 1$) and $0k0$ ($k = 2n + 1$)) was verified by successful structure determination. The single molybdenum atom was located in a three-dimensional Patterson function. The positions of the remaining non-hydrogen atoms were obtained from subsequent Fourier and difference Fourier calculations. Anisotropic full-matrix least-squares refinement of these 25 atoms produced residuals $R = 0.066$ and $R_w = 0.056$.[23] A difference electron density map showed no peak greater

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(23) The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = [2F_o/\sigma(F_o^2)]^2$ and $\sigma(F_o^2) = [\sigma^2(I) + \rho^2 I^2]^{1/2}$ with ρ assigned a value of 0.01. Expressions for the residuals are $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - F_c|)^2/\sum w(F_o)^2]^{1/2}$. Although $R_w < R$ is somewhat unusual, our weighting scheme with $\rho = 0.01$ produces a lower R_w than when $\rho = 0$ is utilized, which leaves $R_w > R$.

Table I

Crystallographic Data for $Mo(MeC{\equiv}CMe)_2(pdtc)_2$

molecular formula	$MoS_4N_2C_{18}H_{20}$
fw	488.57
space group	$P2_1/n$
cell parameters	
a, Å	12.327 (4)
b, Å	12.145 (3)
c, Å	14.184 (3)
β, deg	101.50 (2)
V, Å^3	2088 (2)
ρ(calcd), g/cm^3	1.554
Z	4

Collection and Refinement Parameters

radiation (wavelength, Å)	Mo Kα (0.710 73)
linear abs. coeff, cm^{-1}	10.04
scan type	$\omega/1.67\theta$
scan width, deg	$1.1 + 0.35 \tan \theta$
bkgd	25% of full scan width on both sides
θ limits, deg	$1 < \theta < 25$
quadrant collected	$+h, +k, \pm l$
no. of unique data	3851
no. of data with $I \geq 3\sigma(I)$	1470
R	0.056
R_w	0.041
largest parameter shift/error	0.24
no. of parameters	226
error in an observn of unit wt	1.79

than 0.30 e/Å^3. Idealized hydrogen positions were calculated (d(C–H) = 0.95 Å), and 15 of these 20 hydrogens were located in the last Fourier map. Further refinement allowing the 25 non-hydrogen anisotropic atoms to vary and including the 20 hydrogens in fixed, idealized positions converged with the largest parameter shift to error ratio equal to 0.24 for the final cycle; $R = 0.056$, $R_w = 0.041$.

Results

Syntheses. Synthesis of N,N-dialkyldithiocarbamate derivatives of the type $Mo(R^1C_2R^2)_2(S_2CNR_2)_2$ (R = Me, Et) from $Mo(CO)_3(S_2CNR_2)_2$ requires 1–4 h of reflux in benzene or toluene in the presence of free alkyne. We wish to report the synthesis of analogous complexes containing the electronically unique pyrrole-N-carbodithioate ligand, $Mo(R^1C_2R^2)_2(pdtc)_2$ (pdtc = $^-S_2CNC_4H_4$). Complete conversion of a solution containing 2 equiv of alkyne/mol of $Mo(CO)_2L(pdtc)_2$ (L = THF, ether, CO, or I^-) to the bis(alkyne) product occurs over a period of 4 h at room temperature. Two synthetic routes are suitable for preparation of these bis(alkyne) complexes. The first route requires the initial preparation of $Mo(CO)_3(pdtc)_2$ from $Mo(CO)_4Cl_2$.[19] The saturated $Mo(CO)_3(pdtc)_2$ reagent is dissolved in CH_2Cl_2 and produces an orange solution (THF or ether are also suitable solvents but produce purple solutions). Solution IR spectra at this point show carbonyl stretches indicative of $Mo(CO)_3(pdtc)_2$ in CH_2Cl_2 or $Mo(CO)_2(S)(pdtc)_2$ in coordinating solvents (S = THF or Et_2O). The second route is based on preparation of $[TEA][Mo(CO)_2I(pdtc)_2]$ (TEA = $[(C_2H_5)_4N]^+$) in situ from $[TEA][Mo(CO)_5I]$ by sequential addition of I_2 and $K[S_2CNC_4H_4]\cdot{}^1/_2THF$.[24] Both reaction pathways require 4 h of stirring the molybdenum reagent with 2 equiv of alkyne at room temperature. Addition of the alkyne produces immediate gas evolution and formation of a brown solution characterized by one strong carbonyl stretch, which disappears as the reaction proceeds to completion. Yields ranged from 30 to 50% and were generally higher with the $[TEA][Mo(CO)_5I]$ reagent.

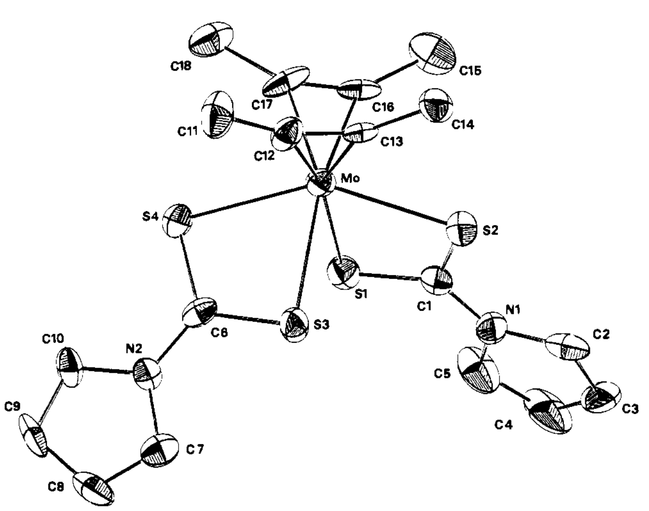

Figure 1. Molecular structure of $Mo(MeC{\equiv}CMe)_2(S_2CNC_4H_4)_2$ with thermal ellipsoids at the 30% probability level.

Table II. Final Atomic Positional Parameters for $Mo(MeC_2Me)_2(pdtc)_2$[a]

atom	x	y	z
Mo	0.2224 (1)	0.1069 (1)	−0.0660 (1)
S(1)	0.1214 (2)	0.1048 (3)	−0.2477 (2)
S(2)	0.0857 (2)	−0.0466 (3)	−0.1021 (2)
S(3)	0.0504 (2)	0.2279 (3)	−0.0640 (2)
S(4)	0.2605 (2)	0.3066 (3)	−0.0927 (2)
N(1)	−0.0313 (6)	−0.0511 (7)	−0.2829 (6)
N(2)	0.0802 (6)	0.4363 (6)	−0.1127 (6)
C(1)	0.052 (1)	−0.002 (1)	−0.218 (1)
C(2)	−0.104 (1)	−0.131 (1)	−0.263 (1)
C(3)	−0.176 (1)	−0.154 (1)	−0.342 (1)
C(4)	−0.151 (1)	−0.091 (1)	−0.415 (1)
C(5)	−0.063 (1)	0.023 (1)	−0.377 (1)
C(6)	0.127 (1)	0.335 (1)	−0.092 (1)
C(7)	−0.028 (1)	0.468 (1)	−0.116 (1)
C(8)	−0.038 (1)	0.574 (1)	−0.136 (1)
C(9)	0.070 (1)	0.616 (1)	−0.143 (1)
C(10)	0.138 (1)	0.528 (1)	−0.134 (1)
C(11)	0.337 (1)	0.227 (1)	0.141 (1)
C(12)	0.282 (1)	0.141 (1)	0.074 (1)
C(13)	0.241 (1)	0.048 (1)	0.072 (1)
C(14)	0.223 (1)	−0.055 (1)	0.126 (1)
C(15)	0.338 (1)	−0.123 (1)	−0.139 (1)
C(16)	0.328 (1)	−0.004 (1)	−0.107 (1)
C(17)	0.379 (1)	0.085 (1)	−0.096 (1)
C(18)	0.478 (1)	0.152 (1)	−0.099 (1)

[a] Numbers in parentheses are the estimated standard deviations of the coordinates and refer to the last significant digits of the preceding numbers.

Previous attempts to synthesize parent bis(acetylene) complexes, $Mo(HC_2H)_2(S_2CNR_2)_2$, with dialkyldithiocarbamates (R = Me, Et)[6] using various experimental techniques produced only traces of the desired bis(acetylene) product. The corresponding pyrrole-N-carbodithioate derivative, $Mo(HC_2H)_2(pdtc)_2$, was isolated in roughly 10% yield after 1 h of acetylene gas sparge through a solution of $Mo(CO)_3(pdtc)_2$ at room temperature. Although difficulty was encountered in purifying the product chromatographically, the sample isolated was adequate for a ^{1}H DNMR study.

Molecular Structure of $Mo(MeC_2Me)_2(pdtc)_2$. The solid-state molecular structure of bis(dimethylacetylene)bis(pyrrole-N-carbodithioato)molybdenum(II) is shown in Figure 1, where the atomic numbering scheme is defined. The geometry of the molecule can best be described as a distorted octahedron with each alkyne occupying one coordination site. The four pyrrole-N-carbodithioate sulfur atoms complete the inner coordination sphere with two sulfur atoms trans to alkynes and the other two sulfurs mutually trans to one another. The two alkynes reside in a cis-parallel configuration. Each alkyne adopts a cis-bent geometry with the methyl groups directed away from the metal. There is no crystallographic symmetry

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[24] Nieter-Burgmayer, S. J.; Herrick, R. S.; Templeton, J. L., unpublished results.

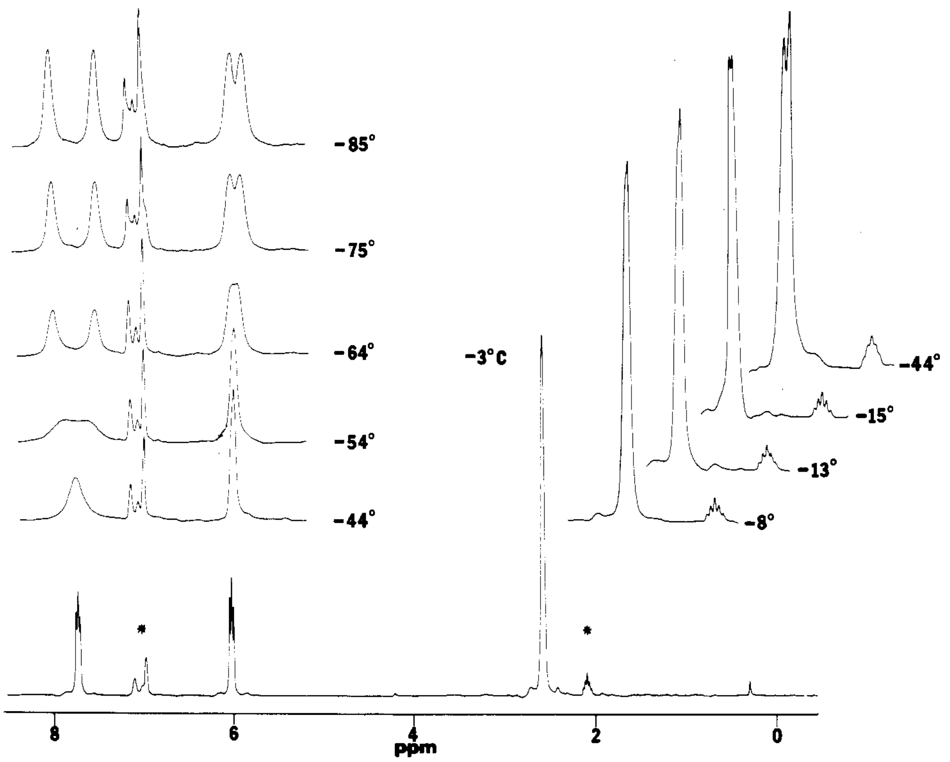

Figure 2. ^{1}H NMR spectra of $Mo(MeC{\equiv}CMe)_2(pdtc)_2$ as a function of temperature in toluene-d_8.

Table III. Selected Bond Distances (Å) in $Mo(MeC_2Me)_2(pdtc)_2$

Mo–C(12)	2.02 (1)	C(6)–N(2)	1.36 (1)
Mo–C(13)	2.06 (1)	C(11)–C(12)	1.48 (1)
Mo–C(16)	2.04 (1)	C(13)–C(14)	1.50 (1)
Mo–C(17)	2.09 (1)	C(15)–C(16)	1.52 (1)
Mo–S(1)	2.631 (3)	C(17)–C(18)	1.48 (1)
Mo–S(2)	2.501 (3)	N(1)–C(2)	1.39 (1)
Mo–S(3)	2.591 (3)	C(2)–C(3)	1.32 (1)
Mo–S(4)	2.513 (3)	C(3)–C(4)	1.37 (2)
C(12)–C(13)	1.24 (1)	C(4)–C(5)	1.38 (2)
C(16)–C(17)	1.25 (1)	C(5)–N(1)	1.36 (1)
S(1)–C(1)	1.65 (1)	N(2)–C(7)	1.39 (1)
S(2)–C(1)	1.70 (1)	C(7)–C(8)	1.32 (1)
S(3)–C(6)	1.71 (1)	C(8)–C(9)	1.45 (1)
S(4)–C(6)	1.69 (1)	C(9)–C(10)	1.35 (1)
C(1)–N(1)	1.38 (1)	C(10)–N(2)	1.39 (1)

Table IV. Selected Bond Angles (deg) in $Mo(MeC_2Me)_2(pdtc)_2$

S(1)–Mo–S(2)	67.8 (1)	C(13)–Mo–C(17)	102.7 (4)
S(1)–Mo–S(3)	77.6 (1)	S(1)–Mo–C(12)	167.0 (3)
S(1)–Mo–S(4)	85.9 (1)	S(1)–Mo–C(13)	150.6 (3)
S(2)–Mo–S(3)	84.4 (1)	S(3)–Mo–C(16)	162.0 (3)
S(2)–Mo–S(4)	145.9 (1)	S(3)–Mo–C(17)	151.1 (4)
S(3)–Mo–S(4)	68.5 (1)	C(11)–C(12)–C(13)	142 (1)
C(12)–Mo–C(13)	35.5 (3)	C(12)–C(13)–C(14)	148 (1)
C(16)–Mo–C(17)	35.1 (4)	C(15)–C(16)–C(17)	142 (1)
C(12)–Mo–C(16)	106.7 (4)	C(16)–C(17)–C(18)	152 (1)

imposed on the molecule although virtual C_2 symmetry is present with the symmetry axis passing through the molybdenum and the midpoint of the plane defined by the four alkyne carbon atoms. Final positional parameters for all non-hydrogen atoms in $Mo(MeC_2Me)_2(pdtc)_2$ are listed in Table II. Selected bond distances and angles are listed in Tables III and IV, respectively.

NMR Properties. Proton NMR spectra of bis(alkyne)bis(pyrrole-*N*-carbodithioato)molybdenum(II) complexes with terminal alkyne ligands show resonances assigned to the alkyne protons between 9.9 and 10.7 ppm. The α- and β-protons of the pyrrole ring are observed as multiplets near 7.6 and 6.3 ppm, respectively. Dynamic ^{1}H NMR studies of $Mo(MeC_2Me)_2(pdtc)_2$ and $Mo(HC_2H)_2(pdtc)_2$ probed stereochemical nonrigidity in these complexes. A sharp singlet is observed at −3 °C for the alkyne methyl groups in the dimethylacetylene derivative (Figure 2). As the temperature is lowered, the signal splits into two equal-intensity singlets with a measured coalescence temperature of 259 K. Similar behavior is observed for both the α- and the β-protons of the pyrrole rings with each multiplet splitting into an equal-intensity pair of multiplets at low temperatures. Coalescence temperatures of 220 and 209 K were measured for the α- and β-protons, respectively. $Mo(HC_2H)_2(pdtc)_2$ displays one resonance due to all four acetylenic protons at room temperature, which broadens and splits into two equal-intensity peaks as the temperature is lowered (T_c = 269 K). Proton-decoupled ^{13}C NMR data for $Mo(MeC_2Me)_2(pdtc)_2$ are listed in the Experimental Section.

Discussion

Reactivity Patterns. The chemistry of $M(CO)_3(dtc)_2$ (M = Mo, W; dtc = $^-S_2CNR_2$) has been extensively studied for dialkyldithiocarbamate derivatives. A common reaction involves facile substitution of one carbonyl ligand with a Lewis base to produce $M(CO)_2L(dtc)_2$ complexes.[25] Replacement of a second carbonyl is difficult although it has been accomplished with 1,2-bis(diphenylphosphino)ethane (probably due to the chelate effect) and also with electron-rich phosphines under forcing conditions.[26] Analogous $M(CO)_3(pdtc)_2$ complexes have recently been prepared and undergo similar Lewis base substitution reactions. A major difference in the chemistry of the pyrrole-*N*-carbodithioate complexes is that bis(phosphine) derivatives of the form $M(CO)(PR_3)_2(pdtc)_2$ are easily accessible. The enhanced reactivity toward substitution of one of the carbonyl ligands in $M(CO)_2L(pdtc)_2$ complexes apparently reflects weaker metal–carbon bonds to the carbonyls in pyrrole-*N*-carbodithioate complexes. Spectroscopic support for less back-bonding to the carbonyl ligands is provided by the higher carbonyl stretches observed in the infrared

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spectra of pyrrole-*N*-carbodithioate complexes relative to those in dialkyldithiocarbamate analogues.[19]

Substitution reactions of M(CO)$_3$(dtc)$_2$ with added alkyne differ from substitution reactions with other nucleophiles as two carbonyls are readily replaced by one alkyne (eq 1).[3]

$$\mathrm{Mo(CO)_3(dtc)_2 + R^1C_2R^2 \rightleftharpoons Mo(CO)(R^1C_2R^2)(dtc)_2 + 2CO(g)} \quad (1)$$

Furthermore, Mo(CO)(R^{1}C$_2$R^2)(dtc)$_2$ complexes are unusual in that the remaining carbonyl ligand is subject to replacement by a second alkyne (eq 2).[3,6] A mechanistic study of this

$$\mathrm{Mo(CO)(R^1C_2R^2)(dtc)_2 + R^1C_2R^2 \rightarrow Mo(R^1C_2R^2)_2(dtc)_2 + CO(g)} \quad (2)$$

substitution chemistry revealed a correlation between higher carbonyl stretching frequencies in the Mo(CO)(R^{1}C$_2$R^2)(dtc)$_2$ derivatives and an increased rate of formation of bis(alkyne) products.[11] This suggests that electron-withdrawing alkynes accelerate loss of the remaining carbonyl ligand. The stretching frequency of the replaceable carbonyl of Mo(CO)(R^{1}C$_2$R^2)(dtc)$_2$ is 130–180 cm^{-1} higher in energy than the frequency of the lone carbonyl in Mo(CO)(PR$_3$)$_2$(dtc)$_2$, which has resisted substitution efforts in our laboratory. This illustrates the alkyne's π acidity and its labilizing effect on carbonyls within the coordination sphere.

Seven-coordinate molybdenum(II) carbonyl complexes containing two pyrrole-*N*-carbodithioate ligands react with alkynes to form bis(alkyne) products at room temperature after an intermediate, believed to be Mo(CO)(R^{1}C$_2$R^2)(pdtc)$_2$, is generated immediately following alkyne addition. Identification of the intermediate is based solely on the presence of a single strong CO stretch in the infrared spectrum of the reaction solution at this point. The carbonyl frequencies exhibited by the Mo(CO)(R^{1}C$_2$R^2)(pdtc)$_2$ species range from 1943 to 1962 cm^{-1} and in each case lie between 10 and 20 cm^{-1} higher than the corresponding frequency for the dimethyldithiocarbamate monocarbonyl mono(alkyne) analogue. Both the increased CO stretching frequencies and the enhanced reactivity toward alkyne replacement of carbonyl ligands provide chemical support for the hypothesis that the pyrrole-*N*-carbodithioate donates less electron density to the metal than comparable dialkyldithiocarbamate ligands because of a substantial decrease in the contribution of resonance form III (vide supra). The enhanced reactivity we observe toward carbonyl substitution processes provides an example of the global reactivity variations that can be induced by electronic modifications of dithiocarbamate ligands in these group 6 derivatives.

The bis(alkyne)bis(pyrrole-*N*-carbodithioato)molybdenum(II) complexes were synthesized by two related but distinct routes. The major disadvantage associated with Mo(CO)$_3$(pdtc)$_2$ as the metal reagent is that it is experimentally difficult to isolate in pure form. In contrast the [TEA][Mo(CO)$_2$I(pdtc)$_2$] reagent can be quantitatively generated in situ by a simple two-step reaction (eq 3 and 4).[27] Bis(alkyne) products

$$\mathrm{[TEA][Mo(CO)_5I] + I_2 \rightarrow [TEA][Mo(CO)_4I_3] + CO(g)} \quad (3)$$

$$\mathrm{[TEA][Mo(CO)_4I_3] + K[S_2CNC_4H_4] \rightarrow [TEA][Mo(CO)_2I(pdtc)_2] + 2CO(g)} \quad (4)$$

form cleanly upon addition of free alkyne to either seven-coordinate reagent (eq 5 and 6).

$$\mathrm{[TEA][Mo(CO)_2I(pdtc)_2] + 2R^1C_2R^2 \rightarrow Mo(R^1C_2R^2)_2(pdtc)_2 + 2CO(g) + [TEA][I]} \quad (5)$$

$$\mathrm{Mo(CO)_3(pdtc)_2 + 2R^1C_2R^2 \rightarrow Mo(R^1C_2R^2)_2(pdtc)_2 + 3CO(g)} \quad (6)$$

The various bis(alkyne) derivatives were isolated as orange crystals with the exception of Mo(*n*-BuC$_2$H)$_2$(pdtc)$_2$, which was isolated as an oil. Synthesis of the parent bis(acetylene) complex, Mo(HC$_2$H)$_2$(S$_2$CNR$_2$)$_2$, with *N*,*N*-dialkyldithiocarbamate ligands had proven elusive in previous preparative efforts, and the trace amounts of Mo(HC$_2$H)$_2$(S$_2$CNMe$_2$)$_2$ that were isolated were insufficient for characterization. The general increase in rate of conversion of the intermediate monocarbonyl mono(alkyne) derivative to the bis(alkyne) product for pyrrole-*N*-carbodithioate complexes is consistent with the rapid reaction of Mo(CO)(HC$_2$H)(pdtc)$_2$ with acetylene at room temperature. This allows isolation of Mo(HC$_2$H)$_2$(pdtc)$_2$ in low yields before decomposition reactions destroy the desired bis(acetylene) product.

Description of the Molecular Structure of Mo(MeC$_2$Me)$_2$(pdtc)$_2$. The inner coordination sphere of bis(dimethylacetylene)bis(pyrrole-*N*-carbodithioato)molybdenum(II) can be described as a pseudooctahedron containing two alkynes in a cis-parallel geometry. The alkynes have a typical cis-bent configuration with a Me—C≡C angle of 146° (average). The alkyne arrangement is analogous to that reported for (η-C$_5$H$_5$)W(CF$_3$C$_2$CF$_3$)$_2$Cl[28] and (η-C$_5$H$_5$)Nb(CO)(PhC$_2$Ph)$_2$[29] and conforms to molecular orbital expectations for such complexes.[2] The four alkyne carbons define a plane (±0.04 Å) and are arranged in a rectangular array with average intraalkyne and interalkyne carbon–carbon distances of 1.244 ± 0.001 and 3.00 ± 0.02 Å, respectively. The interior angles of the alkyne rectangle are all 90 ± 2°. The angle subtended at the metal center by the centroids of the two alkynes is obtuse (99°). The average molybdenum–carbon bond distance is 2.05 Å, similar to the 2.054-Å Mo–C bond length determined for Mo(PhC$_2$Ph)(CNR)$_2$(SR)$_2$ (R = *t*-Bu).[30] The M–C bond distance of π-bound alkynes is reported to correlate with the extent of $\pi_\perp$ to metal dπ donation.[1d,31] The Mo–C bond distance here is longer than that found for Mo(PhC$_2$Ph)(TTP) (TTP = *meso*-tetra-*p*-tolylporphyrin) (1.97 Å average)[1d] and Mo(CO)(PhC$_2$H)(PEt$_3$)$_2$Br$_2$ (1.99 Å average),[1c] which have only one alkyne to provide ligand π-electron density to the metal-based LUMO. It is shorter than the 2.12 Å (average) reported for OMo(MeC$_6$H$_4$O$_2$CC$_2$CO$_2$C$_6$H$_4$Me)(S$_2$CNMe$_2$)$_2$,[8] where the oxo ligand furnishes substantial π-electron density to the LUMO and competes with donation from the alkyne $\pi_\perp$ orbital.

The bis(pyrrole-*N*-carbodithioato)molybdenum fragment parameters are informative when compared to typical dialkyldithiocarbamate geometries. The pair of sulfur atoms which are mutually trans exhibit an average Mo–S distance of 2.51 Å, which is in the range typical for Mo(II) dithiocarbamate complexes (2.45–2.55 Å).[7,8,13,15,25,32] The sulfur atoms trans to the alkynes exhibit a Mo–S distance of 2.61 Å (average); a similar elongation of the M–S bond distance

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(27) The new synthetic route to M(CO)$_3$(dtc)$_2$ from [NR$_4$][Mo(CO)$_5$I] was developed in our laboratory by Dr. Paul Winston and S. J. N. Burgmayer and works for dialkyldithiocarbamate and pyrrole-*N*-carbodithioate complexes of molybdenum and tungsten. Mo(CO)$_3$(pdtc)$_2$ can be generated from [N(C$_2$H$_5$)$_4$][Mo(CO)$_2$I(pdtc)$_2$] by bubbling carbon monoxide through a methylene chloride solution of the iodide adduct for several minutes followed by filtering (under CO) to remove the precipitated ammonium halide salt.

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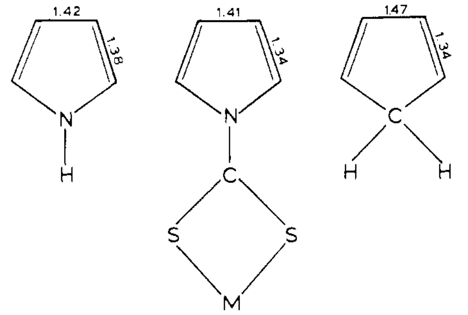

Figure 3. Comparative bond length variations in pyrrole, coordinated pdtc, and cyclopentadiene relevant to the extent of π-electron delocalization.

Table V. Comparison of Differences in Adjacent Ring Bond Lengths in Pyrrole, Pyrrole-*N*-carbodithioate Ligands, and Cyclopentadiene

	[C(3)-C(4)] - [C(2)-C(3)], Å	[C(2)-C(3)] - [N(1)-C(2)], Å
pyrrole[34]	0.035	0.012
pyrrole-*N*-carbodithioate[a]	0.065	0.039
cyclopentadiene[35]	0.127	0.167[b]

[a] Average values of distances present in the solid-state structure of $Mo(MeC_2Me)_2(pdtc)_2$ were used for this analysis. [b] For cyclopentadiene the C(1)-C(2) distance has been used rather than N(1)-C(2).

in $W(CO)(HC_2H)(S_2CNEt_2)_2$ was attributed to the trans effect of bound alkynes.[7] The pyrrole-*N*-carbodithioate bite distances and angles of 2.86 Å (average) and 68° correspond to values found in other (dialkyldithiocarbamato)molybdenum structures.[16]

Each pyrrole-*N*-carbodithioate ligand is nearly planar with internal dihedral angles between the CS_2 and NC_4H_4 fragments of 3 and 7° for the two independent chelates. The near-planarity of these ligands reflects some degree of π interaction between the dithiolate carbon and the pyrrole nitrogen. The pyrrole-*N*-carbodithioate C–N bond distance of 1.37 Å (average) linking the pyrrole and CS_2 fragments falls between normal dialkyldithiocarbamate C–N bond distances (1.30–1.33 Å) and a C–N single-bond distance calculated as the sum of covalent radii (1.47 Å).[33] This indicates that the C–N interaction is significantly decreased in the pyrrole-*N*-carbodithioate ligands. The same conclusion results from comparing pyrrole carbon–carbon and carbon–nitrogen distances in the pdtc ligands with bond lengths in free pyrrole[34] and cyclopentadiene[35] (Figure 3). Note that very similar pdtc structural parameters characterize these chelating ligands in $Fe(pdtc)_3$.[36] If it is kept in mind that the covalent radius of nitrogen is 0.05 Å smaller than that of carbon, free pyrrole displays relatively constant ring bond lengths indicative of aromatic character. Conversely, cyclopentadiene bond lengths alternate as is typical of diene systems. Variations of the average ring bond lengths of the two pyrrole-*N*-carbodithioate ligands lie between those of NC_4H_4 and C_5H_6 (Table V). Using the difference between C(2)–C(3) and C(3)–C(4) bond lengths as a qualitative measure of π delocalization gives the order pyrrole > pyrrole-*N*-carbodithioate > cyclopentadiene, in accord with intuitive chemical expectations.

Spectroscopic Properties. Infrared $\nu(C{\equiv}C)$ stretching frequencies and ^{13}C and ^1H chemical shifts of alkyne carbons and acetylenic protons have previously been used to probe metal–alkyne interactions in alkyne complexes.[4,5] Alkyne complexes containing pyrrole-*N*-carbodithioate chelates exhibit chemical shifts very similar to those reported for $Mo(R^1C_2R^2)_2(S_2CNR_2)_2$ complexes with dialkyldithiocarbamates (R = Me, Et).

Two distinct intramolecular rearrangements were revealed by a variable-temperature proton NMR study of $Mo(MeC_2Me)_2(pdtc)_2$ (Figure 2). The lower energy process involves only the pyrrole protons and exchanges two discrete sets of α- and β-protons such that at the high-temperature limit only one multiplet is observed for all four α-protons and likewise for the β-protons. The barrier for this interconversion, $\Delta G^{\ddagger}$, was calculated to be 10.7 kcal/mol on the basis of the coalescence points and the low-temperature chemical shift differences for both the α- and the β-protons.[37] The presence of a C_2 symmetry axis dictates that the two dithiocarbamates and therefore the two pyrrole rings are symmetry equivalent. At low temperatures the observed spectrum is consistent with a static structure in which the two halves of each pyrrole ring are inequivalent. Two plausible processes that could account for this averaging are rotation around the C–N bond and sulfur dechelation with subsequent rearrangement of the five-coordinate intermediate.[4] The second process is unlikely since the two ends of each alkyne would be expected to exchange during this rearrangement; this contrasts with our experimental results. The low barrier to rotation around the C–N bond (10.7 kcal/mol) is particularly informative when compared to the corresponding barrier for C–N rotation in $Mo(EtC_2Et)_2(S_2CNMe_2)_2$ (18.3 kcal/mol).[6] Even higher $\Delta G^{\ddagger}$ values characterize most other dialkyldithiocarbamate systems.[38] If steric contributions to this barrier are assumed to be negligible, as seems reasonable for Me_2, Et_2, and $(CH)_4$ substituents, the pyrrole-*N*-carbodithioate C–N π bond is roughly only half as strong as in similar dialkyldithiocarbamate complexes.

Two singlets due to the four alkyne groups (methyl for 2-butyne or hydrogen for acetylene) are observed at low temperature for $Mo(RC_2R)_2(pdtc)_2$ complexes. The rearrangements which exchange the two ends of the alkynes are associated with barriers of 13.7 and 13.8 kcal/mol for the bis(dimethylacetylene) and bis(acetylene) derivatives, respectively, for this equal-population two-site exchange process. The ground-state structure of the bis(alkyne) exhibits a cis-parallel arrangement of alkynes and conforms to C_2 symmetry when two symmetrical alkynes are bound. The two ends of each alkyne are distinct with each alkyne related by C_2 symmetry to the other alkyne. Exchange of the two ends of each alkyne is sufficient to cause the observed spectral behavior. The fluxional character of related monocarbonyl mono(alkyne) and bis(alkyne) complexes has been thoroughly investigated with the dynamic NMR observables in each case suggesting rotation of the alkyne around the axis joining the molybdenum and the midpoint of the alkyne. The same phenomenon here would

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exchange the NMR environments of both alkynes by flipping first one alkyne and then the other.[1e,6]

Possible chelate-based rearrangements could also equilibrate both ends of the alkynes. Rearrangement of the octahedral ground-state structure to a trigonal-prismatic intermediate (cf. $Mo(CO)_2(dtc)_2$[15]) would generate a C_{2v} molecular entity with all alkyne units equivalent by symmetry. Alternatively dechelation of a bound sulfur and rearrangement of the five-coordinate species through a C_{2v} geometry could effect the observed exchange (cf. $W(O)(RC_2R)(dtc)_2$).[4] Although neither of these rearrangements can be rigorously excluded, reference to earlier studies of $Mo(RC_2R)_2(dtc)_2$ fluxionality suggests that alkyne rotation is the most reasonable choice for the dynamic process under consideration. Note that either sulfur dechelation or a trigonal-prismatic intermediate structure would be expected to average not only the alkyne termini but also the dithiocarbamate substituents. For the pyrrole case, rotation around the C–N bond at low temperatures conceals any further chelate-based rearrangement with a higher energy barrier. However, for alkyl-substituted dithiocarbamates the different alkyl groups retained their chemical shift integrity even when the alkynes were rapidly averaging on the NMR time scale, thus ruling out dechelation or metal-based global geometric rearrangements for the alkyldithiocarbamate complexes. The similarity of the barriers for averaging of the alkyne environments of the pyrrole-*N*-carbodithioate complexes discussed here and for $Mo(EtC_2Et)_2(S_2CNEt_2)_2$ (15.1 kcal/mol) suggests that an analogous process is occurring in each of these complexes. For this reason we feel alkyne rotation is the most likely mechanism for the high-temperature exchange process observed in $Mo(RC_2R)_2(pdtc)_2$ (R = Me, H).

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Registry No. $Mo(PhC_2Ph)_2(pdtc)_2$, 87101-84-6; $Mo(PhC_2H)_2(pdtc)_2$, 87101-85-7; $Mo(PhC_2Me)_2(pdtc)_2$, 87101-86-8; $Mo(MeC_2Me)_2(pdtc)_2$, 87101-90-4; $Mo(EtC_2Et)_2(pdtc)_2$, 87101-87-9; $Mo(n\text{-}BuC_2H)_2(pdtc)_2$, 87101-88-0; $Mo(HC_2H)_2(pdtc)_2$, 87101-89-1.

Supplementary Material Available: Atomic coordinates used for least-squares analysis (Table VI), weighted least-squares planes and associated deviations (Table VII), dihedral angles between planes (Table VIII), thermal parameters (Table IX), complete bond angles (Table X), and structure factors (Table XI) (20 pages). Ordering information is given on any current masthead page.

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Synthesis, Characterization, and Spectroscopic Studies of Some Metal Derivatives of Hemiporphyrazine

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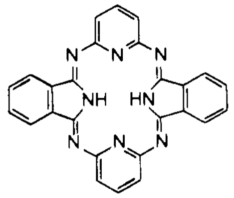
A systematic investigation of the coordination chemistry of the divalent tetraaza macrocycle hemiporphyrazine has been undertaken. Metal derivatives with Co(II), Ni(II), Cu(II), and Zn(II) have been isolated in the form of anhydrous species, water adducts, and complexes of analytical composition $M(hp)(HX)_n$ (HX = HCl, HBr; n = 1, 2). On the basis of their chemical and spectroscopic properties the last compounds are formulated as true adduct derivatives of the M(hp) complexes stabilized by proton interaction with the peripheral nitrogens of the ligand. Upon axial coordination the low-spin Co(hp) undergoes a transition to the high-spin form, whereas Cu(hp) gives low-symmetry derivatives which, in some cases, can be described as tetragonally compressed compounds, with a predominant d_{z^2} ground state. In spite of its apparent similarity to porphyrin-like ligands, hemiporphyrazine is a rather peculiar macrocycle with coordination properties strongly influenced by the weakness and low symmetry of its ligand field.

Introduction

Hemiporphyrazine (hpH_2, Chart I), first synthesized by Linstead some 30 years ago,[1] is a highly conjugated tetraaza macrocyclic ligand with a number of features in common with the much more popular porphyrins (pH_2) and phthalocyanins (pcH_2). Important differences are its low aromatic character,[2] due to the presence of a delocalization pathway of 20 π electrons, and the strong inequivalence of the two pairs of inner nitrogens.

A few metal derivatives of hpH_2 have been reported, but information on their properties is sparse and sometimes misleading. The crystal and molecular structures of the free ligand[3] and its Ni(II)[4] and Ge(IV)[3,5] derivatives have been reported. More recently electrochemical and magnetic data were published for the Mn(II), Co(II), Ni(II), and Cu(II) complexes.[6-8] In striking disagreement with the behavior of the related p and pc complexes typical high-spin magnetic moments were found for Co(hp) and Mn(hp), 4.67 and 5.80 μ_B, respectively. On this basis the authors concluded that hpH_2 is not a suitable porphyrin analogue.

Chart I



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