under 2 atm of CO for 15-30 min. The color of the solution became pale yellow. ^{1}H, ^{31}P, and ^{13}C NMR studies of the resulting solution, together with the IR spectrum of the residue obtained by removal of the solvent, allowed the identification of the organic anhydride $(RCO)_2O$ and of the carbonyls $Ni(CO)_2(PMe_3)_2$ and $Ni(CO)_3(PMe_3)$ as the only detectable products.

X-ray Structure Determination. The air-sensitive crystal of $[Ni(CH_2C_6H_4\text{-}o\text{-}Me)(PMe_3)(\mu\text{-}OH)]_2{\cdot}HNC_4H_2Me_2$ was put in a glass capillary under nitrogen atmosphere and mounted on the goniometer head of an Enraf-Nonius CAD4 diffractometer. Data were collected by using ω-2θ scans and reduced, and a set of 2012 unique reflections was used in subsequent calculations. The analysis of the Patterson map permitted the location of the Ni atoms, the rest of the non-H atoms being located by means of successive cycles of Fourier synthesis. The H atoms were geometrically placed, except the one corresponding to the NH group (extracted from a Fourier difference map). The H atoms corresponding to the OH groups could not be found, and its consideration was omitted. An empirical absorption correction[29] was applied at the end of the isotropic refinement of the non-H atoms but some degree of disorder, nonresolvable from thermal motion, was encountered in the pyrrolyl carbon atoms. The anisotropic refinement converged at $R = 0.057$, using unit weights. A summary of crystal data is given in Table II. All computations were made with the Oxford CRYSTALS package.[30] The atomic scattering factors were taken from ref 31.

Figure 2 shows the geometry of the molecule of **10**. Although the structure has been solved in the triclinic space group $P1$, all attempts to refine it below $R \simeq 20$ (convergence of isotropic refinement) have proved unsuccessful, and thus no crystallographic data are included.

Acknowledgment. Generous support of this work by the Agencia Nacional de Evaluaciôn y Prospectiva is very gratefully acknowledged. P.P. and M.P. thank the Ministerio de Educaciôn y Ciencia for support of a research grant.

Supplementary Material Available: Analytical data for complexes **1**-**11** and ^{1}H, ^{31}P, and ^{13}C NMR data for the pyrrolyl complexes **1**-**5** (Tables A, B, and C), fractional atomic coordinates and thermal parameters for $[Ni(CH_2C_6H_4\text{-}o\text{-}Me)(PMe_3)(\mu\text{-}OH)]_2{\cdot}HNC_4H_2Me_2$ (Tables D and E) (4 pages); observed and calculated structure factors (Table F) (19 pages). Ordering information is given on any current masthead page.

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Preparation of $(\eta\text{-}C_5H_5)W(CO)_2(PPh_3)SR$ and Insertion of CS_2 To Give the Thioxanthates $(\eta\text{-}C_5H_5)W(CO)_2S_2CSR$ (R = $CHMe_2$, CH_2Ph, 4-C_6H_4Me). Crystal Structure of $(\eta\text{-}C_5H_5)W(CO)_2S_2CSCH_2Ph$

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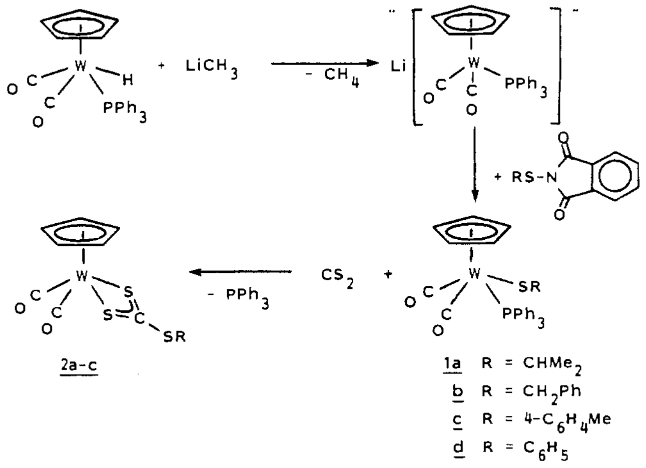
Treatment of $(\eta\text{-}C_5H_5)W(CO)_2(PPh_3)H$ with methyllithium and subsequently with RS(phth) gave $(\eta\text{-}C_5H_5)W(CO)_2(PPh_3)SR$ as a mixture of cis and trans isomers, where phth = phthalimido and R = $CHMe_2$, CH_2Ph, and 4-C_6H_4Me. These isomers react with CS_2 to give the thioxanthate complexes $(\eta\text{-}C_5H_5)W(CO)_2S_2CSR$ wherein the CS_2 has inserted into the W-SR bond. The structure of $(\eta\text{-}C_5H_5)W(CO)_2S_2CSCH_2Ph$ was determined: $C2/c$, $a = 27.106$ (20) Å, $b = 10.050$ (5) Å, $c = 13.108$ (13) Å, $\beta = 66.18$ (7)°, $V = 3266.4$ Å^3, and $Z = 8$. The cis isomer reacted more rapidly than the trans; the reaction was retarded by the presence of free PPh_3 or CO. The implications with respect to the mechanism of CS_2 insertion are discussed.

Introduction

Preparative routes to thiolato complexes of the type $CpW(CO)_3SR$, where Cp = η^5-cyclopentadienide and R = alkyl and aryl, are well developed.[2] As part of our studies on polysulfano tungsten[3] complexes, the triphenylphosphine-substituted complexes $CpW(CO)_2(PPh_3)SR$ were required. Those with R = C_6H_5 and 4-C_6H_4Me have recently been prepared via a complicated photochemical route and were not isolated in the pure state.[4] This paper reports the preparation of the desired complexes by a mild and general route. The presence of the triphenylphosphine ligand renders the complexes susceptible to further reactions. Specifically, it was found that CS_2 easily inserts into the tungsten-thiolate bond to give the thioxanthate complexes $CpW(CO)_2S_2CSR$.

Scheme I



Results

Treatment of $CpW(CO)_2(PPh_3)H$[5] in THF at 0 °C, first with MeLi and subsequently with RS(phth),[6] where phth = phthalimido, gave the complexes $CpW(CO)_2PPh_3SR$ (**1a**-**d**) (Scheme

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Table I. Analytical Data for $CpW(CO)_2(PPh_3)SR$ and $CpW(CO)_2S_2CSR$

compd	no.	yield, %	mp, °C	$\nu(CO)$,[a] cm^{-1}	% C calc	% C found	% H calc	% H found	% S calc	% S found
$CpW(CO)_2(PPh_3)SCHMe_2$	**1a**	46	158–160	1930, 1849[b]	52.35	52.20	4.24	4.17	4.99	4.91
$CpW(CO)_2(PPh_3)SCH_2Ph$	**1b**	69	100–102	1939, 1859[b]	55.67	54.09	3.94	4.16	4.64	4.02
$CpW(CO)_2(PPh_3)S\text{-}4\text{-}C_6H_4Me$	**1c**	71	151–153	1947, 1858[b]	55.67	55.57	3.94	3.84	4.64	4.69
$CpW(CO)_2(PPh_3)SPh$	**1d**	65	168–170	1946, 1869[b]	55.50	54.87	3.72	3.71	4.74	4.78
$CpW(CO)_2S_2CSCHMe_2$	**2a**	58	127–128	1954, 1877	29.96	29.52	2.65	2.68	21.08	20.64
$CpW(CO)_2S_2CSCH_2Ph$	**2b**	67	137–138	1957, 1881	35.74	36.74	2.36	2.36	19.08	19.52
$CpW(CO)_2S_2CS\text{-}4\text{-}C_6H_4Me$	**2c**	45	172–173	1955, 1878	35.74	35.76	2.36	2.51	19.08	18.93

[a] In toluene. [b] Mixture of cis and trans isomers.

Table II. ^1H NMR Data for $CpW(CO)_2(PPh_3)SR$ and $CpW(CO)_2S_2CSR$[a,b]

compd	isomer	C_5H_5	$CHMe_2$	CH_2Ph	CH_3	C_6H_x
$CpW(CO)_2(PPh_3)SCHMe_2$	cis	5.49	2.53[c]		0.92, 1.11	
	trans	5.05[d]	2.81[c]		1.31	
$CpW(CO)_2(PPh_3)SCH_2Ph$	cis	5.09		3.42[e]		7.26[f]
	trans	4.85[g]		3.64		7.26[f]
$CpW(CO)_2(PPh_3)S\text{-}4\text{-}C_6H_4Me$	cis	5.49			2.24	6.93[h]
	trans	5.18[d]			2.28	7.04[h]
$CpW(CO)_2(PPh_3)SPh$	cis	5.50				7.01[f]
	trans	5.13[d]				7.18[f]
$CpW(CO)_2S_2CSCHMe_2$		5.64	4.02[i]		1.44	
$CpW(CO)_2S_2CSCH_2Ph$		5.64		4.42		7.33[f]
$CpW(CO)_2S_2CS\text{-}4\text{-}C_6H_4Me$		5.59			2.40	7.36[j]

[a] In $CDCl_3$ solution; reported in ppm. [b] Phenyl resonances of PPh_3 appeared in the range 7.38–7.44 ppm. [c] Septet, $J(H-H) = 6.6$ Hz. [d] Doublet, $J(P-H) = 2.0$ Hz. [e] Doublet, $J(H-H) = 13.4$ Hz. [f] $x = 5$. [g] Doublet, $J(P-H) = 2.2$ Hz. [h] $x = 4$, quartet, $J(H-H) = 8.0$ Hz. [i] Septet, $J(H-H) = 6.9$ Hz. [j] $x = 4$, quartet, $J(H-H) = 8.4$ Hz.

I). The complexes were isolated as a yellow mixture of cis and trans isomers in 50–70% yield (Table I). Attempts to separate the isomers via column chromatography were only successful in generating samples enriched in one isomer or the other. These samples soon equilibrated in solution (trans/cis ($CDCl_3$): 3.5, **1a**; 2.6, **1b**; 2.8, **1c**). Nevertheless, it was possible to characterize both isomers in solution. They can be clearly differentiated by their NMR spectra (Table II) in which the Cp protons appear as sharp singlets for the cis isomers and as doublets due to coupling with the phosphorus atom ($J = 2$ Hz) for the trans isomers.[7] In addition, the Me protons of the isopropyl derivatives appear as a doublet of doublets for the cis complex, consistent with a diastereotopic environment, and as a single doublet for the trans isomer. The methylene protons of 1b similarly reveal their diastereotopic nature in the cis isomer. As well, enriched cis samples exhibit a strong symmetric carbonyl stretching absorption in the region 1930–1960 cm^{-1} and a weak asymmetric absorption in the region 1850–1870 cm^{-1} of their infrared spectra. Samples enriched in the trans isomer have opposite intensity profiles in their carbonyl absorptions.[7]

The orange-yellow complexes **1a–c** gave red solutions in CS_2 from which the thioxanthate complexes **2a–c** were isolated in 45–67% yield. Although the conversion of **1a–c** to **2a–c** was quantitative, as shown by NMR studies, the appreciable solubility of **2a–c** lowered the yields. Complexes **2b** and **2c** are highly crystalline and interestingly transmit red light and reflect green light with a high luster. The analytical and spectroscopic data for **2a–c** are given in Tables I and II, respectively. The structure of **2b** was determined by an X-ray study and is shown in Figure 1. The crystallographic data and the atomic coordinates are given in Tables III and IV, respectively, while the bond lengths and angles are listed in Table V. The structure is consistent with those reported for similar complexes.[8]

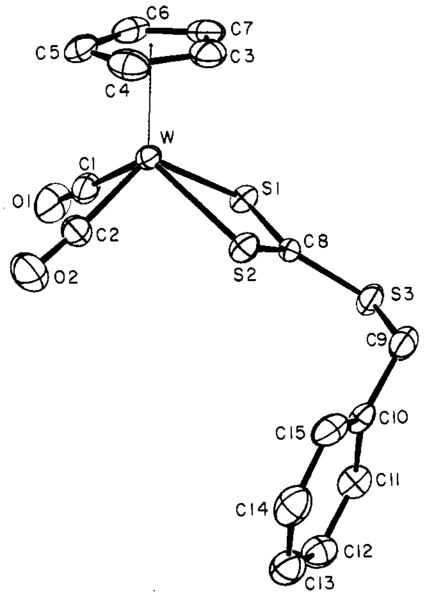

Figure 1. ORTEP view of $CpW(CO)_2S_2CSCH_2Ph$ (**2b**). Selected distances (Å) and angles (deg): W–S1, 2.489 (3); W–S2, 2.481 (2); C8–S1, 1.693 (5); C8–S2, 1.687 (6); C8–S3, 1.735 (5); S3–C9, 1.833 (6); S1–W–S2, 68.5 (6); S1–C8–S2, 111.6 (3).

Table III. Crystallographic Data for $CpW(CO)_2S_2CSCH_2Ph$

chemical formula $C_{15}H_{12}O_2S_3W$	formula weight = 504.29
$a = 27.106$ (20) Å	space group $C2/c$ (No. 15)
$b = 10.050$ (5) Å	$T = 22$ °C
$c = 13.108$ (13) Å	$\lambda = 0.71069$ Å
$\alpha = 90°$	$\rho_{calcd} = 2.051$ g cm^{-3}
$\beta = 66.18$ (7)°	$\mu(Mo\ K\alpha) = 75.93$ cm^{-1}
$\gamma = 90°$	transmission coeff = 22–34%
$V = 3266.4$ Å^3	$R_1 = 0.032$
$Z = 8$	$R_2 = 0.045$

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Table IV. Positional Parameters and Isotropic Thermal Parameters (Å^2) for $CpW(CO)_2S_2CSCH_2Ph$[a,b]

	x	y	z	B_{iso}
W	0.164357 (8)	0.005526 (20)	0.126042 (17)	2.504 (15)
S1	0.07378 (6)	−0.05959 (14)	0.63125 (12)	2.95 (8)
S2	0.12064 (6)	0.19324 (14)	0.58668 (12)	2.99 (8)
S3	0.00644 (6)	0.15652 (16)	0.59694 (14)	3.76 (9)
C1	0.1821 (3)	0.1651 (7)	0.0309 (5)	4.0 (4)
O1	0.19110 (22)	0.2623 (5)	−0.0212 (4)	6.2 (4)
C2	0.22399 (23)	−0.0605 (8)	−0.0088 (5)	3.9 (4)
O2	0.26158 (18)	−0.0972 (6)	−0.0861 (4)	6.0 (3)
C3	0.1476 (3)	−0.0931 (7)	0.3018 (5)	4.0 (4)
C4	0.2036 (3)	−0.0845 (7)	0.2354 (5)	4.4 (4)
C5	0.2171 (3)	0.0525 (8)	0.2187 (6)	4.7 (4)
C6	0.1685 (3)	0.1251 (6)	0.2730 (5)	4.2 (4)
C7	0.1265 (3)	0.0341 (7)	0.3248 (5)	4.2 (4)
C8	0.06538 (21)	0.1020 (5)	0.6055 (4)	2.6 (3)
C9	0.01792 (24)	0.3362 (6)	0.5766 (5)	3.8 (4)
C10	0.05234 (21)	0.3780 (5)	0.4598 (5)	2.8 (3)
C11	0.04118 (24)	0.3399 (6)	0.3672 (5)	3.4 (3)
C12	0.0715 (3)	0.3834 (6)	0.2618 (5)	3.9 (4)
C13	0.1138 (3)	0.4672 (7)	0.2405 (6)	4.0 (4)
C14	0.1262 (3)	0.5092 (6)	0.3300 (8)	4.3 (5)
C15	0.0958 (3)	0.4634 (7)	0.4381 (6)	3.7 (4)

[a] Esd's given in parentheses refer to the last digit(s) of the preceding number. [b] B_{iso} is the arithmetic mean of the principal axes of the thermal vibration ellipsoid.

Table V. Bond Lengths (Å) and Angles (deg) for $CpW(CO)_2S_2CSCH_2Ph$

W–S1	2.489 (3)	C1–O1	1.160 (7)
W–S2	2.481 (2)	C2–O2	1.169 (8)
W–C1	1.968 (6)	C3–C4	1.42 (1)
W–C2	1.967 (7)	C3–C7	1.38 (1)
W–C3	2.377 (6)	C4–C5	1.42 (1)
W–C4	2.289 (6)	C5–C6	1.42 (1)
W–C5	2.267 (6)	C6–C7	1.40 (1)
W–C6	2.312 (6)	C9–C10	1.495 (9)
W–C7	2.400 (7)	C10–C11	1.417 (8)
S1–C8	1.693 (5)	C10–C15	1.392 (9)
S2–C8	1.687 (6)	C11–C12	1.363 (9)
S3–C8	1.735 (5)	C12–C13	1.36 (1)
S3–C9	1.833 (6)	C13–C14	1.41 (1)
		C14–C15	1.40 (1)
S1–W–S2	68.5 (6)	W–S1–C8	89.8 (2)
S1–W–C1	80.0 (2)	W–S2–C8	90.2 (2)
S1–W–C2	122.8 (2)	C8–S3–C9	102.3 (3)
S1–W–C4	140.6 (2)	W–C1–O1	177.0 (6)
S1–W–C5	140.2 (2)	W–C2–O2	175.9 (5)
S1–W–C6	104.1 (2)	C4–C3–C7	108.9 (6)
S2–W–C1	122.7 (2)	C3–C4–C5	107.4 (6)
S2–W–C2	80.2 (2)	C4–C5–C6	107.1 (6)
S2–W–C4	101.2 (2)	C5–C6–C7	108.3 (6)
S2–W–C5	137.4 (2)	C3–C7–C6	108.3 (6)
S2–W–C6	141.3 (2)	S1–C8–S2	111.6 (3)
C1–W–C2	78.7 (3)	S1–C8–S3	121.1 (3)
C1–W–C4	131.5 (3)	S2–C8–S3	127.3 (3)
C1–W–C5	97.1 (3)	S3–C9–C10	115.1 (4)
C1–W–C6	91.3 (3)	C9–C10–C11	122.7 (5)
C2–W–C4	90.5 (3)	C9–C10–C15	120.7 (5)
C2–W–C5	94.9 (3)	C11–C10–C15	116.6 (5)
C2–W–C6	128.7 (3)	C10–C11–C12	122.1 (5)
C4–W–C5	36.3 (3)	C11–C12–C13	121.5 (6)
C4–W–C6	59.5 (3)	C12–C13–C14	118.6 (7)
C5–W–C6	36.1 (3)	C13–C14–C15	120.3 (6)
		C10–C15–C14	120.9 (6)

When a mixture of the isomers of **1a–c** in $CDCl_3$ was treated with CS_2, the signals in the NMR spectrum due to the cis complexes rapidly decreased in intensity followed by a gradual decrease in the intensity of the peaks due to the trans compound. Concomitantly, peaks due to **2a–c** appeared. The reaction of **1a** was much faster than that of **1c**. After 8 h in $CDCl_3$, in the presence of a 270-fold excess of CS_2, the reaction was 95%, 25%, and 1% complete for **1a–c**, respectively. The preparative-scale reactions, run in neat CS_2, proceeded more rapidly. Addition of 1.8 equiv of free PPh_3 slowed the reaction, while 5 equiv slowed it markedly. Purging the sample of **1a** with CO also slowed the reaction; moreover, peaks due to $CpW(CO)_3SR$[9] appeared in the NMR spectrum. Treatment of $CpW(CO)_3SCHMe_2$ in $CDCl_3$ with CS_2 (270-fold excess) gave NMR peaks due to **2a**, but the rate of reaction was much slower than that of **1a**, being only 70% complete after 4 days.

Compound **1a** did not react with CO_2 at ambient temperature and pressure, nor did it react with COS. However, **1a–c** slowly lost PPh_3 in solution to form dimers of the type $[CpW(CO)_xSR]_2$ (x = 1, 2).[10] The dimerization reactions of **1a–c** and their reactions with other electrophiles such as SO_2 are under study.

Discussion

The preparative route to **1a–d** probably involves the anion $CpW(CO)_2PPh_3^-$, itself an interesting species[11] generated by deprotonation of $CpW(CO)_2(PPh_3)H$ by methyllithium. Such an anion would be expected to displace the phthalimido anion from RS(phth) by analogy[12] to the reaction of the anion $CpW(CO)_3^-$ and to chloro anion displacement reactions between the $CpCr(CO)_3^-$ anion and S_xCl_2.[13] Sulfur-transfer reagents of the type RS(phth) are a source of "RS^+" in reactions with thiols to produce disulfides with phthalimide as the byproduct.[6] Deutsch et al.[14] and Lai[15] observed phthalimido anion displacement in reactions of these reagents and coordinated thiolato species. These sulfur-transfer reagents have been shown to react with metal–SH species to generate polysulfano ligands.[3,16] The sulfur–nitrogen bond also oxidatively adds to platinum(0)[15] and titanium(II) species.[17] Thus, they are useful precursors to a variety of metal–sulfur species. The characterization of the chemistry of the $CpW(CO)_2PPh_3^-$ anion is continuing.

The complexes $CpM(CO)_2S_2CSR$ (M = Mo, W; R = Me, Ph) have been prepared previously[18] via treatment of $CpM(CO)_3Cl$ with $M'(S_2CSR)$ (M' = Na^+, NMe_4^+), a fairly general route to such species.[19] The complex where R = Me was also obtained in low yield via treatment of the $CpMo(CO)_3^-$ anion with LiMe and CS_2.[20] Alkali-metal thiolates are known to give thioxanthate salts upon treatment with CS_2.[8a] Insertion of CS_2 into transition-metal thiolates has been reported. The complexes $CpNi(PBu_3)SR$ and $[CpNiSR]_2$ insert CS_2 to give $CpNi(PBu_3)S_2CSR$[21] and $CpNiS_2CSR$,[22] respectively, the latter being unstable. The complex $(PPh_3)_2CuS_2CSEt$ was prepared by dissolving

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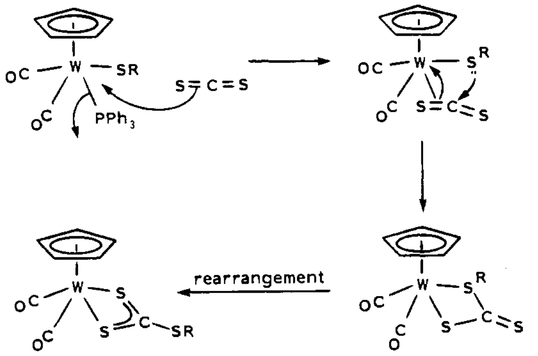
Scheme II



$(PPh_3)_2CuSEt$ in CS_2.[23] A brief note (without supporting evidence) of the reaction of $CpW(CO)_3SR$ (R = Me, Ph) with CS_2 to give $CpW(CO)_2S_2CSR$ appeared 20 years ago.[24] Interestingly, $CpFe(CO)S_2CSR$ loses[19] CS_2 in refluxing toluene to give the dimer $[CpFe(CO)(\mu\text{-}SR)]_2$. It was also reported[19] that CS_2 did not insert into the iron–thiolate bonds of either the latter dimer or the monomer $CpFe(CO)_2SR$. The facile reaction reported here is an interesting analogue of CO_2 insertion into metal–alkoxide bonds[25] and of other "CO_2-like" insertion[26] reactions.

The reactions of **1a–c** with CS_2 were monitored by using NMR spectroscopy. Qualitative observations include the following: (a) the sterically crowded cis isomer reacts more rapidly than the trans, (b) the reaction is accelerated by increasing CS_2 concentration, (c) the reaction is retarded by the presence of free PPh_3 or CO, (d) $CpW(CO)_3SR$ is detected when CO is present, and (e) the reaction of $CpW(CO)_2(L)SCHMe$ is much faster for L = PPh_3 than for L = CO. One could imagine electrophilic attack by either precoordinated or free CS_2 on the coordinated sulfur atom. The latter has been proposed for the insertion of CO_2 into the W–OR bond of $W(CO)_5OR$ anions.[25a] However, that reaction was not inhibited by the presence of free CO. Although the evidence does not completely rule out generation of some **2a–c** via attack by free CS_2, it seems reasonable to suggest that attack by precoordinated CS_2 accounts for most if not all of the **2a–c** produced (Scheme II).

Experimental Section

All reactions were performed in three-necked flasks or appropriately sized Schlenk tubes equipped with a nitrogen inlet. Standard inert-atmosphere techniques[27] were used in all manipulations. Flasks charged with solids were twice evacuated and filled with nitrogen. Solvents were transferred by syringe. Filtrations were performed under nitrogen, and filtrates were reduced to dryness under vacuum (oil pump). The packing and elution of column chromatographs, using solvents as received, were performed in air on activated alumina (Anachemia, 80–200 mesh). Recrystallizations, using distilled solvents, were done under nitrogen in Schlenk tubes or three-necked flasks. A layering technique was employed to recrystallize most compounds, which consisted of dissolving the crude product in a minimal amount of solvent and then carefully adding a precipitating solvent such that it did not mix with the lower layer. The flask was left overnight or longer at −16 °C. The mother liquors were removed via a disposable pipet, and the crystals were washed with the precipitating solvent and dried overnight under vacuum.

Solution infrared (IR) spectra were recorded on a Perkin-Elmer 457 grating infrared spectrophotometer (NaCl, 0.1 mm) and were calibrated by using the 1601.4-cm^{-1} band of polystyrene film. Band positions are accurate to ±2 cm^{-1}. Nujol samples were recorded on an Analect AQS-20 Fourier-transform infrared (FT-IR) spectrophotometer and calibrated by using the red line (632.8 nm) of a He/Ne laser. A triglycine sulfate (TGS) detector was used with a standard resolution of 4 cm^{-1}. Proton nuclear magnetic resonance (^1H NMR) spectra were recorded on Varian XL-200 and Varian XL-300 spectrometers. Chemical shifts (δ) are in ppm units relative to an internal standard, tetramethylsilane (TMS), and are accurate to ±0.02 ppm. Low-resolution mass spectra were measured on a Hewlett-Packard 5980A mass spectrometer at the McGill University Biomedical Mass spectrometery Unit and on a Du Pont 21-492B mass spectrometer in the Otto Maass Chemistry Building with ionizing potentials of 10 or 70 eV. High-resolution and fast atom bombardment (FAB) mass spectra were measured on a ZAB-HS mass spectrometer at the Biomedical Unit with an ionizing potential of 10 eV. All mass spectra were measured with electron impact (EI) ionization unless otherwise stated. Chemical ionization was achieved with an NH_3 source, and FAB mass spectra were measured in a glycerol matrix. Elemental analyses were carried out by Spang Microanalytical Laboratories in Eagle Harbour, MI. Melting point determinations were performed in grease-sealed capillary tubes under nitrogen on a Thomas–Hoover capillary melting point apparatus and are uncorrected.

Tetrahydrofuran (THF), toluene, and hexanes were refluxed over sodium metal and benzophenone and collected by distillation under nitrogen. Dichloromethane was refluxed over P_2O_5 and distilled just prior to use. Absolute ethanol was purged with nitrogen before using. Deuterated solvents (Merck Sharp and Dohme), methyllithium (Aldrich, 1.4 M solution in diethyl ether), and CS_2 (A & C Chemicals) were used as received.

The sulfur-transfer reagents, *N*-(2-propylthio)phthalimide ($Me_2HCS(phth)$), *N*-(phenymethyl)thio)phthalimide ($PhCH_2S(phth)$), and *N*-(phenylthio)phthalimide (PhS(phth)), and *N*–((4-methylphenyl)thio)phthalimide ($4\text{-}CH_3C_6H_4S(phth)$), were prepared according to the method of Back.[6a] Cyclopentadienyltricarbonylhydridotungsten(II) ($CpW(CO)_3H$)[28] and cyclopentadienyldicarbonyl(triphenylphosphine)hydridotungsten(II) ($CpW(CO)_2(PPh_3)H$)[5] were prepared as reported.

A. *cis*- and *trans*-Cyclopentadienyldicarbonyl(triphenylphosphine)(2-propanethiolato)tungsten(II) (1a). The preparations of **1a–d** follow a general procedure, which is described in detail for **1a**. The hydride $CpW(CO)_2(PPh_3)H$ (1.15 g, 2.0 mmol) in THF (40 mL) was treated at 0 °C with an excess of methyllithium (1.6 mL, 2.2 mmol) added slowly by syringe. After approximately 10 min, the clear orange solution became cloudy and a precipitate formed. Five minutes later, a THF solution (20 mL) of *N*-(2-propylthio)phthalimide (0.65 g, 2.9 mmol) was slowly added by cannula to the reaction mixture. The mixture became clear orange, and soon a precipitate formed. The reaction mixture was allowed to warm to room temperature over 3 h while being stirred. The mixture was then filtered through a medium-porosity Schlenk filter (Celite) and the solvent removed under vacuum. The dark orange-brown residue, dissolved in a small volume of CH_2Cl_2, was chromatographed on activated alumina (3 × 50 cm column) with CH_2Cl_2 as eluant. A red-orange band and a subsequent yellow band were collected and evaporated to dryness. Both residues were recrystallized from CH_2Cl_2/hexanes (1:4), each giving a mixture of red (cis) and yellow (trans) crystals of **2a** (combined weight 0.60 g, 46%). Complexes **1b–d** were recrystallized from CH_2Cl_2/ethanol.

B. Cyclopentadienyldicarbonyl(2-propyl thioxanthato)tungsten(II) (2a). The preparations of **2a–c** follow the same procedure as that described in detail for **2a**. Neat CS_2 (20 mL) was added to solid **1a** (0.15 g, 2.3 mmol) to give a blood red solution immediately. After being stirred for 9 h (48 h, **2b–c**), the solution was stripped to dryness (oil pump). The residue was dissolved in 4 mL of CH_2Cl_2 and chromatographed on activated alumina (3 × 40 cm). Elution with CH_2Cl_2 gave one red band, which was collected. Removal of solvent and recrystallization from hexanes gave a dark red powder of **2a** (0.062 g, 58%). Complexes **2b–c** were recrystallized from CH_2Cl_2/hexanes.

C. X-ray Structure Determination. Table III contains details of the crystal parameters, data collection, and structure refinement.[29] Single crystals suitable for crystallographic studies were obtained by recrystallization from CH_2Cl_2/hexanes. The sample chosen, a thick plate, was mounted on a lithium borate fiber with epoxy glue. Preliminary Weissenberg and precession photographs limited the choice of space group to *Cc* or *C*2/*c*. The subsequent solution and refinement of the structure

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were successful in the latter. Intensity data were collected on a second similar crystal, mounted in the same way, after the unit cell data and orientation were obtained from 24 automatically aligned reflections. The data were corrected for Lorentz and polarization effects and scaled by using three reference reflections, whose intensities had been remeasured every 50 cycles.

The structure was solved by using conventional heavy-atom methods. Full-matrix isotropic refinement converged at $R_1 = 0.084$ and $R_2 = 0.125$, after four cycles. At this point, a general absorption correction using the Gaussian summation method was applied and isotropic refinement was continued to a new convergence with $R_1 = 0.072$ and $R_2 = 0.119$. Thereafter, all atoms were assigned anisotropic vibrational parameters and the refinement was continued. It converged at $R_1 = 0.035$ and $R_2 = 0.053$, after five cycles using the block-diagonal approximation. A final four cycles of refinement, with hydrogen atoms placed in calculated positions with the mean isotropic thermal parameter of their carbon atom, yielded the final coordinates reported in Table IV. Tables of thermal parameters and observed and calculated structure factors are included as supplementary material.

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Registry No. *cis*-**1a**, 119997-19-2; *trans*-**1a**, 120056-12-4; *cis*-**1b**, 119997-20-5; *trans*-**1b**, 120056-13-5; *cis*-**1c**, 108366-49-0; *trans*-**1c**, 120056-14-6; *cis*-**1d**, 108366-48-9; *trans*-**1d**, 110043-11-3; **2a**, 120022-20-0; **2b**, 119997-21-6; **2c**, 119997-22-7; $CpW(CO)_2(PPh_3)H$, 33085-24-4; CS_2, 75-15-0; 2-(isopropylthio)phthalimide, 17796-72-4; 2-(benzylthio)phthalimide, 14204-26-3; 2-(4-methylphenylthio)phthalimide, 15199-26-5; 2-(phenylthio)phthalimide, 14204-27-4.

Supplementary Material Available: A full-length table of crystallographic data (Table 6) and a table of anisotropic temperature factors (Table 7) (2 pages); a table of observed and calculated structure factors (Table 8) (15 pages). Ordering information is given on any current masthead page.

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Nuclear Magnetic Resonance Studies of Dicopper(II) Complexes with Binucleating Ligands Containing Imidazoles

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^{1}H NMR spectra of aqueous and nonaqueous solutions of $[Cu_2LX]Y_2$ (L = 2,6-bis[((4-imidazolylethyl)imino)methyl]-4-methylphenolate, 2,6-bis[((4-imidazolylethyl)amino)methyl]-4-methylphenolate; $X = OH^-, Cl^-$; $Y = ClO_4^-, Cl^-$) have been observed, together with the measurement of their solution magnetic susceptibilities. The obtained signals are narrow enough to characterize the species in solution. It has been found that both observed chemical shifts and line widths at half-height decrease as the magnetic moments of the corresponding copper(II) complexes in solution decrease. The line widths of ^{1}H NMR signals are controlled by the population distribution in singlet and triplet states of the complexes. Methanol solutions of $[Cu_2L(OH)]^{2+}$ showed equilibria that are associated with the apical coordination of water molecules: in addition to the water-free complex, two species, $[Cu_2L(OH)(H_2O)]^{2+}$ and $[Cu_2L(OH)(H_2O)_2]^{2+}$, are found by ^{1}H NMR spectra. One of these species was crystallized from methanol solution. The crystal and molecular structures of $[Cu_2L(OH)(H_2O)](ClO_4)_2$ have been determined: space group $P2_1/c$, $a = 7.354$ (4) Å, $b = 21.781$ (19) Å, $c = 16.175$ (8) Å, $\beta = 90.70$ (4)°, $Z = 4$, $R = 0.111$, $R_w = 0.095$. The two Cu atoms in this copper(II) complex are bridged by the oxygen atoms of the phenolate and hydroxy groups. The axial position at one Cu atom is occupied by a water molecule, while another Cu has no apical ligand. The coordinate geometries around the two Cu atoms are distorted tetragonal-pyramidal and square-planar.

Introduction

Interest[2] in copper proteins has centered on the design, preparation, and characterization of small-molecular binuclear copper(II) complexes, which offer insight into the coordination chemistry of copper(II) systems in laccase, oxyhemocyanin, and so on. Among a vast body of binuclear copper(II) complexes that have so far been synthesized,[3,4] the complexes containing imidazoles are of marked importance in relation to the copper center of native proteins because a histidyl imidazole is one of the most probable coordinated ligands.[2]

In addition to single-crystal X-ray structural information, the characterization of binuclear copper(II) complexes in solution is of significance. Although NMR spectroscopy has been successfully used to investigate the structural and bonding properties of metal complexes,[5] there are few NMR studies of paramagnetic copper(II) complexes because signals are usually broadened out.[6] On the other hand, antiferromagnetically coupled copper(II) complexes are expected to give relatively narrow NMR signals.[7-10] However, there are still few reports that demonstrate the usefulness of NMR spectra of binuclear copper(II) complexes in solution.

The purpose of this work was to obtain NMR spectra of some binuclear copper(II) complexes having imidazoles. On the basis of these spectra, the structures in solution and equilibria are discussed, which are simultaneously compared with the X-ray crystallographic molecular structure determined in this paper. Finally, the relationship between the structure and NMR parameters is examined.

Experimental Section

Materials. Copper(II) salts were commercially available and utilized after recrystallization. 2-Hydroxy-5-alkylisophthalaldehydes (alkyl = methyl, ethyl) were prepared by the method of Okawa.[11] Histamine free base was isolated from histamine dihydrochloride (Sigma Chemical Co.) by the usual procedure.[12]

Deuterated solvents were purchased from Merck and wako Pure Chemical Industry Ltd. In order to obtain rigorously dry methanol, CD_3OD was refluxed over Mg and distilled before use. Acetone-d_6 was treated with molecular sieves. Both solvents were purified under pure

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