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THIOKETONE COMPLEXES OF CHROMIUM, MOLYBDENUM, AND TUNGSTEN CARBONYLS

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Summary

A series of thioketone complexes of the type $M(CO)_5(S{=}CR_2)$, where M = Cr, Mo or W, and R = Me, Et or Ph, have been prepared by the reaction of $M(CO)_5I^-$ with Ag^+ in the presence of the ketone ($O = CR_2$) and H_2S. Coordination to the metal stabilizes thioketones such as thioacetone which, otherwise, is unstable and polymerizes rapidly Infrared, ^1H and ^{13}C NMR spectra of the compounds are consistent with the ligands being coordinated through the sulfur atom The $W(CO)_5(S{=}CR_2)$ complexes react with MeCN, I^-, N_3^- and $C_6H_{11}NH_2$ (in CCl_4) to give the thioacetone-displaced products, $W(CO)_5L$ With $C_6H_{11}NH_2$ in pentane another product is obtained which apparently results from amine addition to the thioketone ligand This compound reacts with MeI and Et_3O^+ to give the dialkyl sulfide complexes, $W(CO)_5(SMe_2)$ and $W(CO)_5(SEt_2)$

Introduction

Unlike their oxygen analogs, many thioketones [1] are unstable and oligomerize to trithianes at or below room temperature, e g


(1)

For this reason, few metal complexes of thioketones have been reported, and those are derived from stable thioketones such as cycloheptatrienethione [2], adamantanethione [3], thiobenzophenone [3], and substituted thiobenzophenones [4] No complexes of unstable thioketones have been described. The purpose of the present study was to determine whether or not unstable thioketones could be stabilized by coordination to a metal, and then to examine the reactivity of the coordinated thioketone ligand.

Results and discussion

Syntheses

Thioacetone complexes, $M(CO)_5(S{=}CMe_2)$, of Cr, Mo, and W were prepared by first generating $M(CO)_5(O{=}CMe_2)$ from $M(CO)_5I^-$ [5] followed by addition of H_2S

$$[NEt_4][M(CO)_5I] + AgBF_4 \xrightarrow[\text{acetone}]{-72^\circ C} AgI\downarrow + [NEt_4]BF_4 + M(CO)_5(O{=}CMe_2) \quad (2)$$

$$M(CO)_5(O{=}CMe_2) + \tfrac{3}{2}\,H_2S + AgBF_4 \xrightarrow[\text{acetone}]{-72^\circ C} M(CO)_5(S{=}CMe_2) + H_2O + \tfrac{1}{2}\,Ag_2S\downarrow + HBF_4 \quad (3)$$

The Cr and W thioacetone complexes were obtained in 67 and 74% yields, respectively (Table 1), while the Mo analog was too unstable to be isolated, although its formation under the reaction conditions was supported by its infrared, NMR and visible spectra (Tables 2, 4 and 7).

Although the mechanism of step 3 in the above preparation has not been established, it is known [1] that thioketones form at −80° to −40°C when H_2S is bubbled into an acidic solution of the ketone. In the present reaction, the second mole of $AgBF_4$ would provide the acidic conditions ($2\,Ag^+ + H_2S \rightarrow Ag_2S + 2\,H^+$) required for thioacetone formation. If only sufficient $AgBF_4$ to precipitate AgI is used, no $M(CO)_5(S{=}CMe_2)$ complex is obtained. Thus the reaction may take place in the following 2 steps

$$O{=}CMe_2 + H_2S + H^+ \rightarrow S{=}CMe_2 + H_3O^+ \quad (4)$$

$$M(CO)_5(O{=}CMe_2) + S{=}CMe_2 \rightarrow M(CO)_5(S{=}CMe_2) + O{=}CMe_2 \quad (5)$$

While this is a reasonable mechanism for the formation of these complexes, it does not exclude other possible pathways, e.g., via H_2S attack on coordinated

TABLE 1

PHYSICAL AND ANALYTICAL DATA FOR THE $M(CO)_5L$ COMPLEXES

L	M	Color	M.p. (°C)	Yield (%)	Analyses (Found (calcd.) (%))		
					C	H	S
$SCMe_2$	Cr	Orange	63—65	67	36.07 (36.09)	2.27 (2.28)	11.34 (12.04)
$SCMe_2$	W	Red	67—70	74	23.92 (24.14)	1.36 (1.52)	7.52 (8.05)
SCMeEt	W	Orange	oil	9	not determined		
SCMePh	W	Purple	109—110	73	34.02 (33.93)	1.84 (1.76)	7.51 (6.97)
$SCPh_2$	W	Blue	54—56 [a]	9	41.16 (41.40)	2.00 (1.93)	
$[N_3]$	W	Yellow	149—151 [a]	47		[b]	

[a] Decomposed. [b] Nitrogen analysis 6.04(6.56).

acetone in $M(CO)_5(O{=}CMe_2)$ or via formation of $M(CO)_5SH_2$ or $M(CO)_5SH^-$ which subsequently reacts with acetone.

Of the $M(CO)_5(S{=}CMe_2)$ complexes, $W(CO)_5(S{=}CMe_2)$ was the most stable showing no decomposition in CS_2 solution in an O_2 atmosphere during 2 h at room temperature Stabilities of the $[M(CO)_5(S{=}CMe_2)]$ complexes toward H_2O were determined as follows: three ^1H NMR tubes were charged with 1 drop of H_2O and ca 0.4 ml $DCCl_3$ To tube 1, impure $Mo(CO)_5(S{=}CMe_2)$ (ca 0 03 mmol) was added, to tube 2, $Cr(CO)_5(S{=}CMe_2)$ (ca. 0 03 mmol) was added, and to tube 3, $W(CO)_5(S{=}CMe_2)$ (ca 0 03 mmol) Spectra recorded immediately on mixing exhibited a singlet for the methyl groups of $[M(CO)_5(S{=}CMe_2)]$ and a broad singlet which was assigned to the protons of H_2O After standing at room temperature for 5 h, the initial methyl singlet of $Mo(CO)_5(S{=}CMe_2)$ disappeared, and a new singlet (τ 7 83 ppm) for uncoordinated acetone appeared in the spectrum After 24 h, a spectrum of the sample containing $Cr(CO)_5(S{=}CMe_2)$ showed the initial methyl singlet with a slight amount of acetone The $W(CO)_5(S{=}CMe_2)$ sample spectrum showed no change after 24 h Samples which indicated acetone formation also developed a black precipitate The acetone formation possibly results from H_2O attack on the coordinated thioacetone carbonyl carbon atom with subsequent rearrangement to H_2S and the ketone

For the preparation of $W(CO)_5$(thioketone) complexes other than $W(CO)_5(S{=}CMe_2)$, tetrahydrofuran (THF) was used as solvent to generate the reactive intermediate $W(CO)_5(THF)$, which was subsequently converted to the thioketone product These syntheses were carried out as follows

$$[NEt_4][W(CO)_5I] + AgBF_4 \xrightarrow[THF]{-40^\circ C} AgI\downarrow + [NEt_4]BF_4 + W(CO)_5(THF) \qquad (6)$$

$$W(CO)_5(THF) + R^1R^2C{=}O + 3/2\ H_2S + AgBF_4 \xrightarrow[THF]{-40^\circ C} W(CO)_5(S{=}CR^1R^2) + H_2O + 1/2\ Ag_2S + HBF_4 \qquad (7)$$

$(R^1 = Me\ \ R^2 = Et\ \ R^1 = Me\ \ R^2 = Ph\ \ R^1 = R^2 = Ph)$

Due to the insolubility of $[NEt_4][W(CO)_5I]$ in THF at lower temperatures, the reactions were performed at −40° C The stability of $W(CO)_5(S{=}CMePh)$ was comparable to $W(CO)_5(S{=}CMe_2)$, whereas $W(CO)_5(S{=}CPh_2)$ was substantially less stable, as found previously [3] The yields of $W(CO)_5(S{=}CPh_2)$ and $W(CO)_5(S{=}CMeEt)$ were also much lower than for $W(CO)_5(S{=}CMe_2)$ (Table 1) All of the thioketone complexes are soluble in both polar and non-polar solvents such as hydrocarbons, diethyl ether, $CHCl_3$, acetone and acetonitrile

Unlike aliphatic thioketones which can exist as monomers at very low temperatures, aliphatic thioaldehydes (RHC=S) rapidly trimerize [1] even at low temperatures. Our attempts to prepare complexes of monomeric thioaldehydes were also unsuccessful Pentacarbonyl(2,4,6-trimethyltrithiane)chromium(0), $[Cr(CO)_5(SCMeH)_3]$, was formed when $[NEt_4][Cr(CO)_5I]$ and MeCHO were treated according to equations 6 and 7 The solution IR spectrum of the product was consistent with reported values for $[Cr(CO)_5(SCMeH)_3]$ [6], and it showed a parent ion peak in its mass spectrum

Spectral properties

By analogy with thioamide structures, e g , $W(CO)_5$(thioamide) [7], the thio-

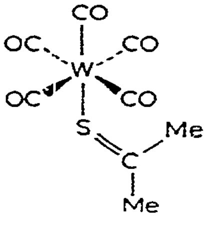
TABLE 2

CO STRETCHING FREQUENCIES (cm^{-1})[a] FOR THE M(CO)$_5$(S=CR$_2$) COMPLEXES

L	M	Solvent	$A_1(2)$	B_1	E	$A_1(1)$
SCMe$_2$	Cr	pentane	2062	1980	1953	1946
SCMe$_2$	Mo[b]	pentane	2069		1956	1940
SCMe$_2$	W	pentane	2068	1975	1950	1938
SCMeEt	W	hexane	2069	1979	1949	1937
SCMePh	W	pentane	2062	1974	1949	1938
[N$_3$]	W[c]	CH$_2$Cl$_2$	2071		1915	1845
SCPh$_2$	W	pentane	2064	1973	1951	1935

[a] Relative band intensities $A_1(2)$ weak B_1 very weak E strong $A_1(1)$ medium [b] Impure compound [c] $\nu(N_3)$ 2037 cm^{-1} (medium intensity)

ketone complexes presumably have structures of the type illustrated for W(CO)$_5$(S=CMe$_2$) (I) The X-ray structural investigation [8] of Cr(CO)$_5$(S=CMe$_2$) con-



(I)

firms this structure Consistent with this C_{4v} local symmetry are the three (2A$_1$ and E) observed and predicted ν(CO) absorptions In addition, a very weak forbidden B$_1$ absorption is observed (Table 2) In Table 3 are reported the non-carbonyl stretching absorptions. Of these absorptions, we tentatively assign the band in the 1253—1255 cm^{-1} region to the ν(C=S) mode This assignment is based on similar assignments in (adamantanethione)pentacarbonyltungsten(0) [3], 1130 cm^{-1}, and dichlorobis(cycloheptatrienethione)palladium(II) [2], 1050 and 1062 cm^{-1}, and on the position (1269 cm^{-1}) of ν(CS) in free thioacetone [9,10] The ~15 cm^{-1} decrease in ν(CS) upon coordination is similar to decreases observed for the previously reported thioketone complexes [2,3]

TABLE 3

INFRARED BANDS (cm^{-1})[a] EXCEPT ν(CO) FOR THE M(CO)$_5$(S=CR$_2$) COMPLEXES

L	M	Solvent	
SCMe$_2$	Cr	CCl$_4$	2924vw, 2890vw, 2838vw, 2827vw, 1352vw, 1319vw, 1295vw 1255w[b], 688w, 654w
SCMe$_2$	W	CCl$_4$	2973vw, 2938vw 2907vw, 2856vw 2843vw, 1342vw, 1319vw 1295vw, 1253w[b] 933vw 698 vw
SCMePh	W	CCl$_4$	2933vw 1360vw 1325vw, 1295vw, 1253w[b], 688vw 662vw
SCPh$_2$	W[c]	CCl$_4$	1319vw, 1295vw, 1250w[b]

[a] Relative band intensities vw very weak w weak [b] ν(C=S) tentative assignment [c] Recorded only in 1350 to 600 cm^{-1} region

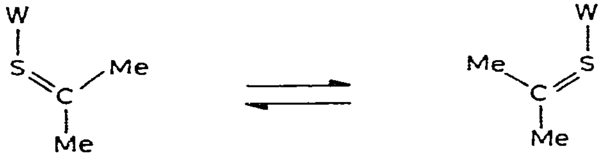
TABLE 4

^{1}H CHEMICAL SHIFTS FOR THE $M(CO)_5(S{=}CR_2)$ COMPLEXES

L	M	Solvent	τ (ppm) [a] [b]
$SCMe_2$	Cr	$DCCl_3$	7 22 (s) (—) $C\underline{H}_3$
$SCMe_2$	Mo [c]	$DCCl_3$	7 23 (s) (—) $C\underline{H}_3$
$SCMe_2$	W	$DCCl_3$	7 32 (s) (—) $C\underline{H}_3$
SCMeEt	W	CS_2	8 66 (t) (3) $CH_2C\underline{H}_3$, 7 33 (s) (3) $C\underline{H}_3$, 7 07 (q) (2) $C\underline{H}_2CH_3$
SCMePh	W	$DCCl_3$	7 00 (s) (3) $C\underline{H}_3$, 2 33 (m) (5) Ph
$SCPh_2$	W	$DCCl_3$	2 50 (m) (—) Ph

[a] Chemical shifts (splittings) (relative intensities) assignment [b] Abbreviations for splitting s singlet t triplet q quartet m multiplet [c] Impure compound

In Table 4 are given the ^{1}H NMR positions and assignments for the protons in the thioketone complexes If the thioacetone complexes have structure I, the two types of methyl groups (*cis* and *trans* to the W) should occur as separate resonances. However, only one resonance was observed in both the ^{1}H and ^{13}C NMR (Table 5) spectra of $Cr(CO)_5(S{=}CMe_2)$ and $W(CO)_5(S{=}CMe_2)$. For $W(CO)_5(S{=}CMe_2)$, only a singlet in the ^{1}H NMR spectrum was observed even down to —100° C using the Fourier transform spectrometer. This suggests that there is either rapid rotation around the C=S bond or inversion at the sulfur atom which wags the $=CMe_2$ group back and forth as shown in structures II and III



(II) (III)

For a similar process in the *S*-arylthiouronium cations, $(Me_2N)_2C{=}SAr^+$, the rates are fast (a coalescence temperature of —92° C for Ar = Ph) and the fluxionality is believed to occur by rotation around the C=S (or C^+—S^-) bond [11], rather than by inversion

TABLE 5

^{13}C CHEMICAL SHIFTS FOR THE $M(CO)_5(S{=}CR_2)$ COMPLEXES

L	M	Solvent	ppm downfield from TMS [a,b]
$SCMe_2$	Cr	$DCCl_3$	—247 5 (s), $\underline{C}{=}S$ —223 0 (s) *trans*-$\underline{C}O$ —214 5 (s) *cis* $\underline{C}O$ —39 4 (s), $\underline{C}H_3$
$SCMe_2$	W	$DCCl_3$	—244 9 (s), $\underline{C}{=}S$ —201 5 (s) *trans*-$\underline{C}O$ —196 2 (s), *cis* $\underline{C}O$ —39 9 (s) $\underline{C}H_3$
SCMePh	W	$DCCl_3$	—221 5 (s) $\underline{C}{=}S$ —202 1 (s), *trans*-$\underline{C}O$, —196 2 (s) *cis*-$\underline{C}O$ —144 2 (s), —133 3 (s), —128 9 (s), —126 6 (s) Ph —37 0 (s), $\underline{C}H_3$

[a] Chemical shifts (splittings) assignment [b] Abbreviation for splitting s, singlet

The equivalence of the methyl groups in $W(CO)_5(S{=}CMe_2)$ could also result from a rapid dissociation and recombination of the thioacetone ligand. This possibility is unlikely since no significant replacement of thioacetone in $W(CO)_5(S{=}CMe_2)$ occurs in 20 minutes when the complex is dissolved in CH_3CN at room temperature. On refluxing the solution, however, $W(CO)_5(NCMe)$ is obtained in good yield (see below).

The ^{13}C NMR spectra of the complexes are reported and assigned in Table 5. Mann and Todd have independently reviewed the ^{13}C NMR spectra of metal carbonyl complexes [12]. Assignments for the thioketone complexes were based on assignments in related complexes and on the relative integrated intensities. The *trans*-carbonyl carbon resonances were downfield relative to those of the *cis*-CO groups (relative intensities 1/4) in the new compounds. A similar effect is observed for other $[(L)M(CO)_5]$ complexes and agrees with the C_{4v} symmetry [13].

Kalinowski and Kessler [14] have used equation 8 to estimate ^{13}C NMR chemical shifts of thiocarbonyl carbon atoms from chemical shifts of their carbonyl

$$\delta(C{=}S) = 1.45\,\delta(C{=}O) + 46.5 \text{ ppm} \tag{8}$$

analogs. Using −206.0 ppm [15] for $Me_2C{=}O$ and −197.6 ppm for $Me(Ph)C{=}O$, the chemical shifts of $Me_2C{=}S$ and $Me(Ph)C{=}S$ should be −252.2 ppm and −240 ppm, respectively. When coordinated in the $M(CO)_5(S{=}CR_2)$ complexes, the chemical shifts (Table 5) are observed to be upfield from those calculated for the uncoordinated thioketone.

In Table 6 mass spectra of the new compounds are reported. The fragmentation patterns demonstrate a facile loss of five carbonyls. The observation of the $WCPh_2^+$ and $Ph_2CCPh_2^+$ fragments in the mass spectrum of $[W(CO)_5(S{=}CPh_2)]$ was the only evidence for a metal-carbene complex (e.g., $W{=}CPh_2$) resulting from the $[W(CO)_5(S{=}CR_2)]$ complexes.

Ultraviolet-visible absorptions of the thioketone compounds are given in Table 7. Like the free thioketones [1], the complexes are highly colored (Table 1), closely paralleling the colors of the free ligands.

Reactions of $W(CO)_5(S{=}CR_2)$

On stirring $W(CO)_5(S{=}CMePh)$ at room temperature in CH_2Cl_2 solvent for 18 h, there was no reaction with electrophiles such as MeI or $[Et_3O]BF_4$. Refluxing the same complex with EtI (b.p. 72° C) for 2 h gave a 61% yield of $W(CO)_6$. Unlike $W(CO)_5(SPMe_2Ph)$ which reacts [16] with MeI at room temperature to give $[Me_2PhPSMe][W(CO)_5I]$, the coordinated thioacetophenone is quite unreactive toward electrophiles.

With nucleophiles, however, the thioketone was observed to be displaced easily. Thus, on refluxing a red solution of $W(CO)_5(S{=}CMe_2)$ in MeCN (b.p. 81° C) for 25 minutes, the yellow $W(CO)_5(NCMe)$ was isolated in 85% yield. It was identified by its infrared [17] and ^1H NMR (τ 7.62 ppm in $DCCl_3$) spectra.

The reaction of $W(CO)_5(S{=}CMe_2)$ with $[Et_4N]I$ in methanol at room temperature for 20 minutes gave an 88% yield of $[Et_4N]W(CO)_5I$, which was identified by comparison of its infrared spectrum with a sample prepared by the literature procedure [18].

The azide salt, $[(Ph_3P)_2N]N_3$, reacted with $W(CO)_5(S{=}CMe_2)$ in acetone at

TABLE 6

MASS SPECTRA[a] OF THE [$W(CO)_5L$] COMPLEXES

$W(CO)_5SCMe_2$ [b]	$Cr(CO)_5SCMe_2$ [c]	$W(CO)_5SCPhMe$ [b]	$W(CO)_5SCPh_2$ [b]	$W(CO)_5SEt_2$ [b,d]
400—386 (100) *A*	268—264 (51) *B*	462—458 (78) *C*	524—520 (40) *D*	416—412 (100) *E*
372—368 (22) *A* — CO	212—208 (19) *B* — C_2O_2	406—402 (96) *C* — C_2O_2	468—464 (43) *D* — C_2O_2	388—384 (66) *E* — CO
344—340 (50) *A* — C_2O_2	184—180 (33) *B* — C_3O_3	378—374 (100) *C* — C_3O_3	440—436 (49) *D* — C_3O_3	360—356 (68) *E* — C_2O_2
316—312 (21) *A* — C_3O_3	156—152 (52) *B* — C_4O_4	350—346 (30) *C* — C_4O_4	384—380 (24) *D* — C_5O_5	332—328 (14) *E* — C_3O_3
288—284 (7) *A* — C_4O_4	128—124 (100) *B* — C_5O_5	322—318 (87) *C* — C_5O_5	352—348 (55) *D* — C_5O_5S	304—300 (15) *E* — C_4O_4
74 (33) *A* — C_5O_5W	114—110 (39) *B* — $C_6H_2O_5$	136 (9) *C* — C_5O_5W	322 (30) $Ph_2C{=}CPh_2$	90 (11) *E* — C_5O_5W
59 (11) *A* — $C_6H_3O_5W$	99—95 (17) *B* — $C_7H_5O_5$	121 (9) *C* — $C_6H_3O_5W$	326—322 (24) *D* — $C_{13}H_{10}S$	75 (16) *E* — $C_6H_3O_5W$
	86—82 (73) *B* — $C_8H_6O_5$	103 (9) *C* — C_5HO_5SW	298—294 (29) *D* — $C_{14}H_{10}OS$	
	74 (14) *B* — C_5O_5Cr		270—266 (13) *D* — $C_{15}H_{10}O_2S$	
	59 (14) *B* — $C_6H_3CrO_5$		198 (100) *D* — C_5O_5W	
	54—50 (76) *B* — $C_8H_6O_5S$		166 (48) *D* — C_5O_5SW	
	39 (13) *B* — $C_5H_3CrO_5S$		77 (11) *D* — $C_{12}H_5O_5SW$	

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[a] Mass to charge ratio (relative intensity) fragments$^+$ are underneath there are several abundant isotopes of W and Cr [b] Ionization potential 16 eV with vacuum lock [c] Ionization potential 70 eV with vacuum lock [d] Absolute mass ^{182}W 411 9732 ± 0 0021

TABLE 7

ULTRAVIOLET-VISIBLE SPECTRA OF THE $M(CO)_5(S{=}CR_2)$ COMPLEXES

L	M	Solvent	nm[a]					
$SCMe_2$	Cr	pentane	470 (5940)	371 (2510)	341 (sh)	294 (3190)	248 (30 300)	227 (34 400)
$SCMe_2$	Mo[b]	pentane	443	360	348	311	254	233
$SCMe_2$	W	pentane	448 (9010)	359 (4420)	326 (3060)	288 (4830)	246 (64 300)	229 (72 100)
SCEtMe	W	hexane	444 (11 000)	356 (6760)	322 (6140)	280 (10 100)	243 (65 200)	
SCPhMe	W	pentane	552 (13 000)	360 (3310)	318 (7760)	304 (9800)	250 (39 800)	225 (33 900)
$SCPh_2$	W	pentane	553 (9470)	361 (2600)	325 (7510)	310 (8970)	248 (35 800)	225 (40 800)

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[a] Extinction coefficients in mol^{-1} cm^{-1} in parentheses. [b] Impure compound

room temperature for 30 minutes to give a 51% yield of $[(Ph_3P)_2N][W(CO)_5N_3]$. The infrared spectrum and melting point (Tables 1 and 2) were identical to those of a sample of this azido complex [19] prepared independently via the reaction of $W(CO)_5I^-$ with $[(Ph_3P)_2N]N_3$

A 10-fold excess of cyclohexylamine, $C_6H_{11}NH_2$, reacted with $W(CO)_5(S{=}C\text{-}MePh)$ in CCl_4 at room temperature to give a 70% yield of $W(CO)_5(NH_2C_6H_{11})$, which was identified by its infrared [20] and mass spectra An identical reaction carried out in pentane solution produced an unstable "yellow precipitate" which was stable at —25° C but decomposed to brown-black tars at room temperature in vacuo Although it was not possible to characterize the "yellow precipitate", it probably is formed via amine addition to the thiocarbonyl carbon atom. A similar yellow precipitate resulted from the reaction of $W(CO)_5(S{=}CMe_2)$ with $C_6H_{11}NH_2$ When stirred in pentane with MeI at room temperature for 1 5 h, this latter yellow precipitate gave the yellow oil $W(CO)_5(SMe_2)$ [21] in 47% yield based on the $W(CO)_5(S{=}CMe_2)$ originally used Similarly the reaction of the yellow solid with $[Et_3O]BF_4$ in CH_2Cl_2 at 25° C gave a 64% yield of $W(CO)_5(SEt_2)$, which was not sufficiently stable for elemental analysis but has infrared (2070w, 1937s, and 1927m in hexane), mass, and proton NMR (τ 8 67 ppm triplet for $C\underline{H}_3$, τ 7 15 ppm quartet for CH_2, in $CDCl_3$) spectra expected [21] for this complex (The complex was also prepared from $W(CO)_5I^-$ by treatment with $AgBF_4$ and SEt_2 in acetone at —72° C) When stirred in diethyl ether under an atmosphere of gaseous HBr for 15 minutes, the yellow precipitate regenerated the original thioketone complex, $W(CO)_5(S{=}CMe_2)$, in 42% yield

Like the unstable "yellow precipitate" obtained from the amine reaction, we were unable to characterize products of the reactions of $W(CO)_5(S{=}CMe_2)$ with other nucleophiles such as MeLi, i-Pr_2NLi or CH_3ONa.

Experimental

Infrared spectra were obtained using a Perkin—Elmer 337 spectrophotometer Band positions were calibrated with polystyrene. Varian A-60 and Perkin—Elmer R20B spectrometers were used to obtain ^1H NMR spectra. An internal standard, tetramethylsilane, was added to the solutions containing the sample, and peak positions are reported in τ (ppm) Solution ^{13}C NMR spectra were obtained with a Bruker HX-90 E Fourier Transform Spectrometer employing proton decoupling Deuterated solvents served as the internal lock and peak positions are reported in δ (ppm) relative to tetramethylsilane Tris(acetylacetonate)-chromium(III) (25 mg) was added to the sample solutions to improve the relative intensities [12] of the carbonyl carbon absorptions.

Mass spectra were obtained employing a Varian Mat CH4 spectrometer Each sample spectrum was recorded with ionizing potentials of 18 and 70 eV Bausch and Lomb Spectronic 505 and Cary 14 spectrophotometers were used to obtain solution ultraviolet and visible spectra Elemental analyses were performed by Chemalytics, Inc , Tempe, Arizona.

Reaction flasks were dried at 110° C for at least 12 h and flushed with nitrogen immediately before use. Manipulations of reaction mixtures and residues were performed under an atmosphere of nitrogen. Acetone was dried over drierite for 24 h and purged with a stream of nitrogen. Tetrahydrofuran was distilled from lithium aluminum hydride under a nitrogen atmosphere. Methylene chloride, hexanes, carbon disulfide, and n-pentane were stored over activated, type 4A molecular sieves.

Tetraethylammonium pentacarbonyl(iodo)-chromate(0), -molybdate(0), and -wolframate(0), $[NEt_4][M(CO)_5I]$, were prepared by the method of Abel, et al [18]. Bis(triphenylphosphine)imminium azide, $[(Ph_3P)_2N]N_3$, precipitated when a saturated aqueous solution of NaN_3 was added to a saturated aqueous solution of $[(Ph_3P)_2N]Cl$, it was dried under vacuum. Silver tetrafluoroborate, $Ag[BF_4]$, and triethyloxonium tetrafluoroborate, $[Et_3O][BF_4]$, were stored and handled in a glove bag which contained P_4O_{10} as a desiccant. Hydrogen sulfide, H_2S, was passed through a drying tube containing P_4O_{10}. All other reagents and solvents were used as received.

Preparation of pentacarbonyl(2-thiopropanone)-Group VIA metal(0) complexes, $[M(CO)_5(S{=}CMe_2)]$ ($M = Cr$, Mo, and W)

A solution of 1.0 mmol of $[NEt_4][M(CO)_5I]$ and 10 ml of acetone in a 50 ml flask was cooled in a Dry Ice/isopropyl alcohol bath (—72° C) for 8 minutes. A solution of 2.0 mmol of $Ag[BF_4]$ in acetone was added to the yellow solution. An immediate precipitation of yellow AgI occurred. Gaseous H_2S was condensed into the cold mixture for 45 minutes. As the flask warmed to room temperature, volatile components of the black mixture were removed in vacuo. The residue was treated with pentane and the red-orange soluble portion was filtered with suction through a frit of medium porosity. Successively concentrating the filtrate under a stream of nitrogen and cooling to —40° C gave the products. The compounds, $[M(CO)_5(SCMe_2)]$, were identified by their elemental analyses and spectra which are reported in the Tables.

Preparation of pentacarbonyl(thioketone)tungsten(0) complexes, $[W(CO)_5(S{=}CR^1R^2)]$ ($R^1 = Me$, $R^2 = Ph$, $R^1 = Me$, $R^2 = Et$, $R^1 = R^2 = Ph$)

These compounds were prepared in a manner similar to that used for $[W(CO)_5(S{=}CMe_2)]$ with the following modifications. Reactions were conducted in THF and cooled in Dry Ice/calcium chloride/water slurry (—40° C). A 10 to 20 fold excess of the appropriate ketone was introduced to the reaction mixture prior to the addition of H_2S. After the residue was treated with pentane, the solution portion was chromatographed on a silica gel (60—200 mesh) column (2 × 36 cm), eluting successively with 200 ml of pentane, 100 ml of 40% CS_2/pentane (v/v), 100 ml of 80% CS_2/pentane, and 200 ml of CS_2. Collection of the colored eluate, concentration in vacuo, and cooling to —78° C gave the products, $[W(CO)_5(SCR^1R^2)]$. They were characterized by their elemental analyses and spectra as given in the Tables.

Preparation of bis(triphenylphosphine)imminium pentacarbonylazidowolframate(0), $[(Ph_3P)_2N][W(CO)_5N_3]$ [19]

To a 10 ml flask were successively added 0.138 g (0.238 mmol) of $[(Ph_3P)_2N]N_3$, 8 ml of acetone, and 0.139 g (0.239 mmol) of $[NEt_4][W(CO)_5I]$. After stirring for 48 h, the yellow mixture was filtered through a frit of medium porosity with suction, giving a white solid (m.p. 295—300° C, $[NEt_4]I$) and a yellow filtrate. Dilution of the filtrate with pentane and recrystallization of the resultant yellow solids from acetone/ether/hexane gave the compound, $[(Ph_3P)_2N][W(CO)_5N_3]$ Percentage yield, melting point, analytical data, and spectra for this compound are recorded in Tables 1 and 2

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