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Conversion of Dithiocarboxylato to Dithioacetylphosphorane and Thioacylphosphorane Ligands

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The reaction of the η^2-dithiocarboxylato compound η^5-$C_5H_5(CO)_2W(\eta^2$-$S_2CCH_3)$ with trimethylphosphine provides at -50 °C high yields of a tungstadithiacyclobutane ylide complex (**2a**). However, reactions of aryl substituted η^2-dithiocarboxylato complexes η^5-$C_5H_5(CO)_2W(\eta^2$-$S_2CR)$ (R = C_6H_5, $C_6H_4CH_3$) give in boiling acetone tungstathiacyclopropane complexes **3b**,**c** and $Me_3P{=}S$. The structures of the new cyclic compounds were determined by spectroscopic investigations and, in the case of **3b**, additionally by X-ray analysis. Crystal data for **3b** are as follows: orthorhombic space group *Fdd*2 with lattice constants a = 31.713 (10) Å, b = 26.004 (7) Å, c = 8.468 (2) Å, and Z = 16.

Introduction

The successful addition of Lewis acids to neutral carbyne complexes can either be frontier orbital or charge controlled, resulting in an electrophilic attack on the metal or, in the other case, in a reaction at the carbyne carbon atom.[1,2] Thus, protonation of cyclopentadienyl-substituted carbyne complexes of molybdenum and tungsten opens an easy access to carbene,[3-5] acyl,[6,7] or alkyne[8] complexes. With sulfur, selenium, or cyclohexene sulfide dithioacetato and diselenoacetato complexes[9,10] are formed in a 2-fold addition reaction, whereas the corresponding osmium carbyne complex $Cl(CO)(PPh_3)_2Os{\equiv}CTol$ adds only one chalcogen atom to give η^2-chalcogenoacyl compounds.[11]

Toward trimethylphosphine the dithioacetato complexes of tungsten show a pronounced reactivity to afford tungstadithiacyclobutane or tungstathiacyclopropane complexes, depending upon the substituent on the former carbyne carbon atom.

Results and Discussion

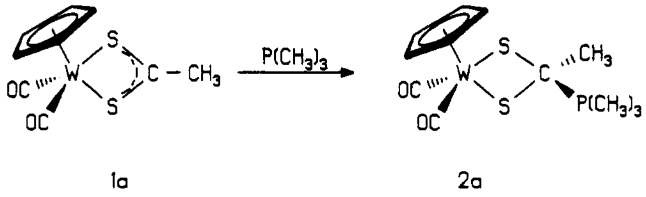
The addition of trimethylphosphine to the sp^2 carbon of dicarbonyl(η^5-cyclopentadienyl)(η^2-dithioacetato)tungsten (**1a**) generates in excellent yield the neutral ylide complex dicarbonyl(η^5-cyclopentadienyl)(η^2-dithioacetylphosphorane)tungsten **2a** (Scheme I).

The red-violet, diamagnetic compound is soluble in dichloromethane or acetone. In solution decomposition already starts at -50 °C. Transition-metal complexes containing similar S_2CHPR_3 ligands are known for cobalt and rhodium.[12-14] The analogous manganese compounds[15] show a pronounced tendency for dimerization, whereas the corresponding iron complexes loose hydrogen.[16]

In polar solvents an equilibrium is observed between **2a** and **1a**; temperature decrease and an increase of the trimethylphosphine concentration favor **2a**.

In contrast to **1a** the dicarbonyl(η^5-cyclopentadienyl)(η^2-dithioacetato)tungsten complexes with aryl substituents **1b** and **1c** show an unexpected reaction behavior toward trimethylphosphine: At room temperature neither a phosphine addition nor a carbonyl/phosphine substitution occurs. However, upon boiling in acetone a combined phosphine addition/sulfur cleavage takes place to provide new η^2-thioacylphosphorane complexes in high yields. The eliminated sulfur is intercepted by trimethylphosphine in the form of $Me_3P{=}S$ (Scheme II).

Scheme I



Scheme II

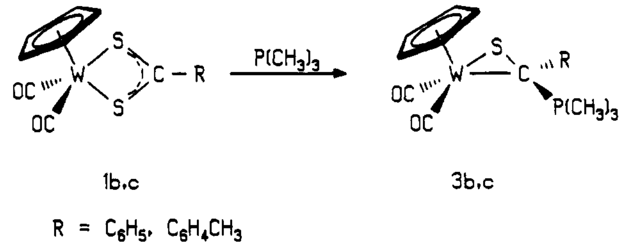


Table I. IR Spectra (cm^{-1}) of 1a, 2a, 3b, and 3c in the ν(CO) Region

compd	medium	W-CO
1a	CH_2Cl_2	1955 vs, 1872 vs
2a	CH_2Cl_2	1910 vs, 1803 vs
	KBr	1902 vs, 1802 vs
3b	CH_2Cl_2	1893 vs, 1786 vs
3c	CH_2Cl_2	1892 vs, 1785 vs

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Table II. $^{13}C\{^1H\}$ NMR Spectral Data of 2a, 3b, and 3c (δ) at 20 °C

compd	WCO	$C_6H_{4/5}$	C_5H_5	C	CH_3	$P(CH_3)_3$
2a	259.3		96.2	69.4 (d, 55.2)[a]	35.1 (d, 14.7)[b]	5.5 (d, 57.2)[a]
3b	253.9 (d, 10.4),[c] 240.7	146.1–126.1	93.8	29.2 (d, 58.6)[a]		12.3 (d, 58.6)[a]
3c	253.9 (d, 9.3),[c] 240.7	142.8–127.9	93.9	29.0 (d, 58.7)[a]	21.0 (d, 1.5)[c]	12.2 (d, 58.7)[a]

[a] $^1J(^{31}P-^{13}C)$ (Hz). [b] $^2J(^{31}P-^{13}C)$ (Hz). [c] $^nJ(^{31}P-^{13}C)$ (Hz).

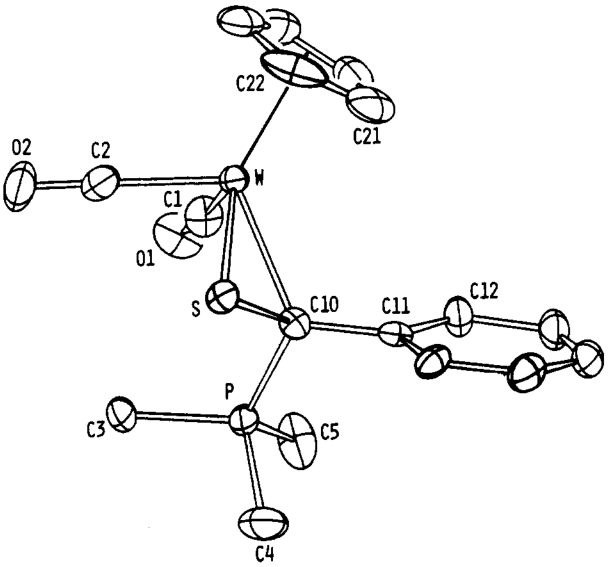

Figure 1. Structure of **3b** solved by conventional Patterson and Fourier techniques.

The orange, diamagnetic compounds **3b** and **3c** are soluble in acetone and dichloromethane and stable at room temperature.

The composition and structure of these compounds were confirmed by elemental analysis, infrared, proton, carbon-13, and phosphorus NMR, and mass spectroscopy, in the case of **3a**, by an additional X-ray analysis.

The infrared spectra of **2a**, **3b**, and **3c** (Table I) in dichloromethane (**2a** recorded in the presence of additional trimethylphosphine) display in the ν(CO) region two signals for the metal carbonyl groups at lower wavelengths according to the addition of the nucleophile PMe_3.

In the carbon-13 NMR spectra of **2a**–**3b** (Table II) the quarternary carbon atoms occur as doublets due to coupling with the added phosphorus of the PMe_3 group. The $^{31}P-^{13}C$ coupling constants of 55–59 cycles underline the ylidic character of the positively charged four-coordinated phosphorus atom.[17] The chemical shifts of the two carbonyl ligands in **3b**,**c** differ by as much as 13 ppm. In the case of **2a** only one carbonyl resonance is recorded in agreement with its C_s symmetry.

The mass spectroscopic investigation display for **3b** (FD) and **3c** (CI) molecular ions at $m/z = 502$ and 516. In the case of **2a** (EI) only the signals for the starting compounds **1a** and trimethylphosphine are recorded due to a thermal decomposition of **2a** in the solid.

The structure of **3b** was solved by conventional Patterson and Fourier techniques and is shown in Figure 1. The atomic positional and thermal parameters are listed in Table III and the intramolecular distances and angles in Table IV.

Table III. Positional and Thermal Parameters for 3b

atom	*x*	*y*	*z*	*U*(eq), Å^2
W	0.18013 (1)	0.15248 (1)	0.00000 (0)	0.031 (1)
S	0.17999 (5)	0.16570 (9)	0.28758 (23)	0.036 (1)
P	0.19386 (5)	0.05562 (7)	0.27992 (25)	0.036 (1)
O(1)	0.2281 (2)	0.0585 (3)	−0.1386 (8)	0.069 (4)
O(2)	0.2754 (2)	0.1813 (3)	0.0191 (10)	0.079 (5)
C(1)	0.2080 (3)	0.0931 (3)	−0.0826 (11)	0.049 (5)
C(2)	0.2394 (2)	0.1714 (3)	0.0128 (11)	0.050 (4)
C(3)	0.2493 (2)	0.0679 (3)	0.2591 (12)	0.047 (4)
C(4)	0.1850 (3)	0.0460 (5)	0.4883 (19)	0.082 (7)
C(5)	0.1831 (3)	−0.0055 (3)	0.1846 (19)	0.076 (8)
C(10)	0.1598 (2)	0.1056 (3)	0.2134 (8)	0.032 (4)
C(11)	0.1147 (2)	0.0930 (3)	0.2370 (11)	0.036 (4)
C(12)	0.0932 (2)	0.0600 (3)	0.1349 (10)	0.045 (5)
C(13)	0.0507 (2)	0.0456 (4)	0.1582 (13)	0.056 (6)
C(14)	0.0290 (2)	0.0672 (3)	0.2883 (12)	0.052 (5)
C(15)	0.0497 (3)	0.1012 (4)	0.3865 (14)	0.058 (6)
C(16)	0.0913 (2)	0.1143 (3)	0.3655 (10)	0.042 (4)
C(21)	0.1106 (3)	0.1800 (8)	−0.0464 (17)	0.109 (11)
C(22)	0.1363 (5)	0.2265 (5)	−0.0301 (14)	0.089 (9)
C(23)	0.1629 (4)	0.2245 (4)	−0.1565 (14)	0.072 (7)
C(24)	0.1560 (3)	0.1817 (4)	−0.2418 (13)	0.066 (6)
C(25)	0.1251 (4)	0.1543 (4)	−0.1772 (17)	0.076 (8)

Table IV. Intramolecular Distances (Å) and Angles (deg) in 3b[a]

W–S	2.459 (2)	S–W–C(1)	118.4 (3)
W–C(1)	1.913 (9)	S–W–C(2)	84.9 (3)
W–C(2)	1.947 (8)	S–W–C(10)	44.5 (2)
W–C(10)	2.272 (7)	S–W–Z	117.7 (3)
W–C(21)	2.352 (14)	C(1)–W–C(2)	77.1 (4)
W–C(22)	2.387 (13)	C(1)–W–C(10)	89.3 (3)
W–C(23)	2.357 (11)	C(1)–W–Z	121.9 (4)
W–C(24)	2.314 (10)	C(2)–W–C(10)	111.4 (3)
W–C(25)	2.302 (12)	C(2)–W–Z	122.1 (4)
W–Z	2.03 (1)	C(10)–W–Z	121.9 (4)
O(1)–C(1)	1.199 (11)	W–S–C(10)	62.2 (2)
O(2)–C(2)	1.169 (11)	W–C(10)–S	73.2 (2)
S–C(10)	1.801 (7)	W–C(10)–P	118.1 (3)
P–C(10)	1.781 (7)	W–C(10)–C(11)	120.1 (5)
P–C(3)	1.796 (8)	S–C(10)–P	107.9 (4)
P–C(4)	1.804 (13)	S–C(10)–C(11)	119.2 (5)
P–C(5)	1.816 (11)	W–C(1)–O(1)	174.6 (7)
C(10)–C(11)	1.481 (10)	W–C(2)–O(2)	178.1 (7)

The bond distances from tungsten to the cyclopentadienyl ring and to the carbonyl ligands are similar to those found for other organometallic tungsten complexes. Within the tungsten–sulfur–carbon ring, the W–S [2.459(2) Å] and the S–C(10) [1.801(7) Å] bond distances are comparable to those reported for the tungstathiacyclopropane system in $[\mathrm{HB(pz)_3}](\mathrm{CO})_2\overline{\mathrm{W{-}CH(S}}\mathrm{Me)PPh_2}$[18] [W–S 2.440 (9); S–C 1.80 (3) Å] and for the η^2-thiocarbene complexes $[\mathrm{Cp(CO)_2}\overline{\mathrm{W{=}C(S}}\mathrm{Me)Ph}][\mathrm{BF_4}]$[19] [W–S 2.429 (1); S–C 1.821 (8) Å]. The tungsten–carbon bond distance corresponds to a single bond, like in $[\mathrm{HB\ (pz)_3}]$-$(\mathrm{CO})_2\overline{\mathrm{W{-}CH(S}}\mathrm{Me)PPh_2}$[18] [2.22 (3) Å] or $\mathrm{Cp(CO)_3W{-}C_6H_5}$[20] [2.32 (2) Å]. The P–C(10) bond length [1.781 (7) Å] is slightly shorter than the corresponding value in

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$[\mathrm{Cp(CO)(PMe_3)}\overline{\mathrm{WAs(Me)_2C(Tol){=}C(PMe_3)O}}]\mathrm{I}$[21] [1.819 (11) Å] or $\mathrm{(CO)_4Re(\mu^2\text{-}CO)(\mu^2\text{-}C(Ph)PMe_3)W(CO)_4}$ (1.92 Å).[22]

Experimental Section

Reagents and Solvents. All manipulations are carried out under purified nitrogen atmosphere with use of conventional Schlenk techniques. The solvents diethyl ether and pentane were distilled over sodium/potassium and dichloromethane was distilled over sodium/lead alloy (E. Merck, D-6100 Darmstadt), and acetone was stored over type 4A molecular sieves and degassed with nitrogen prior to use. Dichloromethane-d_2 was purchased from Merck; trimethylphosphine was synthesized according to the literature.[23]

Spectroscopic Methods. The IR spectra were obtained on a Nicolet 5 DX FT-IR spectrometer, using a CaF_2 cell. Proton, carbon-13, and phosphorus NMR spectra were recorded in dichloromethane-d_2 solutions at 270.2 or 67.8 MHz, respectively, on a JEOL JNM-GX 270 spectrometer; chemical shifts are reported relative to $CDHCl_2$ (5.32 ppm for ^1H) and CD_2Cl_2 (53.8 ppm for ^{13}C). The ^{31}P NMR spectra were obtained on a JEOL JNM-GX 270 spectrometer in dichloromethane-d_2 at 109.4 MHz with the chemical shifts relative to 85% H_3PO_4. Mass spectra were recorded with a Varian MAT 311A or a Finnigan MAT 90 instrument, using EI, CI, and FD techniques.

Preparation of 1,1-Dicarbonyl-1-(η^5-cyclopentadienyl)-3-methyl-3-(trimethylphosphoranyl)-1-tungsta-2,4-dithiacyclobutane (2a). In a typical procedure 1 mL of trimethylphosphine was added to 0.4 g (1 mmol) of **1a** in approximately 50 mL of ether at −50 °C. Within 1 h the red color of the solution slowly turned to violet, and the crude product was completely precipitated with pentane. Further purification by washing with pentane yielded, after drying under vacuum at 0 °C, 0.46 g (96%) of **2a**, a purple powder. Anal. Calcd for $C_{12}H_{17}O_2PS_2W$: C, 30.52; H, 3.63; W, 38.93. Found: C, 30.36; H, 3.71; W, 38.62. ^1H NMR (dichloromethane-d_2, 20 °C, 270.2 MHz): δ 5.68 (s, C_5H_5), 1.76 (d, J = 12.7 Hz, $P(CH_3)_3$), 1.52 (d, J = 17.1 Hz, CH_3). ^{31}P NMR (dichloromethane-d_2, 20 °C, 109.4 MHz): δ 32.2 (s, $CP(CH_3)_3$). MS (EI): m/z 396 (parent cation − PMe_3), 368 (parent cation − PMe_3 − CO), 340 (parent cation − PMe_3 − 2CO), 76 (trimethylphosphine).

Preparation of 1,1-Dicarbonyl-1-(η^5-cyclopentadienyl)-3-phenyl-3-(trimethylphosphoranyl)-1-tungsta-2-thiacyclopropane (3b). A solution of 30 mL of acetone containing 0.26 g (0.57 mmol) of the dithiocarboxylato complex **1b** and 1 mL of trimethylphosphine was refluxed for 72 h, yielding a red-brown solution. The solution was evaporated to dryness under reduced pressure, and the residue was washed with pentane. After subliming the side product $Me_3P{=}S$ under high vacuum at 80 °C, the orange residue was recrystallized from dichloromethane at −20 °C, yielding 0.23 g (76%) of orange crystals of **3b**. Anal. Calcd for $C_{17}H_{19}O_2PSW$: C, 40.66; H, 3.81; S, 6.38. Found: C, 40.55; H, 3.91; S, 6.44. ^1H NMR (dichloromethane-d_2, 20 °C, 270.2 MHz): δ 7.46–7.10 (m, C_6H_5), 5.01 (s, C_5H_5), 1.55 (d, J = 12.2 Hz, $P(CH_3)_3$). ^{31}P NMR (dichloromethane-d_2, 20 °C, 109.4 MHz): δ 33.6 (s, $CP(CH_3)_3$). MS (FD): m/z 502 (parent cation).

Preparation of 1,1-Dicarbonyl-1-(η^5-cyclopentadienyl)-3-(4-methylphenyl)-3-(trimethylphosphoranyl)-1-tungsta-2-thiacyclopropane (3c). The analogous reaction of 1.42 g (3.01 mmol) of **1c** in 100 mL of acetone with 1 mL of trimethylphosphine yielded, after purification and drying under vacuum, 1.38 g (89%) of **3c**, an orange powder. Anal. Calcd for $C_{18}H_{21}O_2PSW$: C, 41.88; H, 4.10; S, 6.21. Found: C, 41.94; H, 4.37; S, 6.11. ^1H NMR (dichloromethane-d_2, 20 °C, 270.2 MHz): δ 7.33–7.04 (m, C_6H_4), 5.01 (s, C_5H_5), 2.31 (s, CH_3), 1.53 (d, J = 12.2 Hz, $P(CH_3)_3$). ^{31}P NMR (dichloromethane-d_2, 20 °C, 109.4 MHz): δ 33.4 (s, $CP(CH_3)_3$). MS (CI): m/z 516 (parent cation), 460 (parent cation − 2CO).

X-ray Diffraction Study of 3b. A crystal fragment with dimensions 0.2 × 0.2 × 0.4 mm was sealed in a Lindemann glass capillary. X-ray data were collected by using Philips PW 1100 diffractometer and graphite-monochromated Mo K_α radiation (λ = 0.71069 Å) at room temperature. A least-squares calculation with the diffractometer settings for 34 reflections gave the following parameters for the orthorhombic unit cell: a = 31.713 (10), b = 26.004 (7), c = 8.468 (2) Å. The space group, consistent with the systematic extinction and the solution of the structure, if *F2dd* (No. 43). For $C_{17}H_{19}O_2PSW$ with M = 502.22 g/mol and Z = 16, d_{calcd} = 1.911 g/cm^3.

Intensity data ($\theta/2\theta$ scans, $\theta_{\max}$ = 23°) were collected corresponding to a monoclinic unit cell ($\pm h,+k,+l$) and space group *Cc*. The *hkl* values were later transformed accordingly to the *Fdd*2 unit cell. An Lp and in a later stage (after refinement of the structure with isotropic temperature factors) an empirical absorption correction (μ = 65.3 cm^{-1}) was applied.[24]

The structure was solved by the Patterson method. The R indices after refinement with anisotropic temperature factors were R = 0.024 and $R_w(F)$ = 0.027. A total of 2510 reflections was used in the calculations. The H atoms of the phenyl group could be seen in a final ΔF map; however, H atoms were not included in the calculations. The highest peak in a final ΔF map was 0.76 e·Å^{-3}.[25] The SHELX program package was used for the calculations.[26]

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Supplementary Material Available: Tables of geometric calculations and final coordinates and thermal parameters for **3b** (5 pages); a listing of observed and calculated structure factors for **3b** (15 pages). Ordering information is given on any current masthead page.

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[25] Additional data concerning the structure determination may be obtained from the Fachinformationszentrum Energie, Physik, Mathematik, D-7514 Eggenstein-Leopoldshafen 2, Germany, by quoting the Registry No. CSD 55003, the name of the authors, and the journal citation.

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