Inorganica Chimica Acta, 222 (1994) 77–84

Carbonyl carbene coupling on cationic η^2-carbene complexes of molybdenum and tungsten

C. Ogric, J. Ostermeier, M. Heckel, W. Hiller and F.R. Kreißl*
Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstraße 4, 85747 Garching (Germany)

(Received January 24, 1994)

Abstract

The reaction of η^2-phosphino- or η^2-thiocarbene complexes of molybdenum and tungsten with sodium thiocyanate provides high yields of metalla(phospha/thia)bicyclo[1.1.0]butanone compounds. The structures of the new bicyclic complexes were determined by spectroscopic investigations and, in the case of **6b**, additionally by X-ray analysis.

Key words: Crystal structures; Carbene coupling; Molybdenum complexes; Tungsten complexes; Carbene complexes

Introduction

Since the discovery of the transition metal carbene [1] and carbyne [2] complexes, many other complexes with a metal carbon multiple bond have been synthesized by the classical routes of Fischer, by Schrock's method or by way of new preparative approaches [3–5]. The explorations of the metal carbon multiple bond have fascinated many research groups, and carbene as well as carbyne complexes have become increasingly important in theory, synthesis and catalytic research. Carbene as well as carbyne complexes can be conveniently classified into Fischer-type complexes with the metal not in its highest possible oxidation state and into Schrock-type complexes with the metal in a considerably high oxidation state.

In agreement with theoretical calculations by Fenske [6, 7] and Hofmann [8] cyclopentadienyl substituted carbyne complexes [9–11] $\mathrm{Cp(CO)LM{\equiv}CR}$ ($\mathrm{M=Mo}$, W; $\mathrm{L=CO}$, $\mathrm{PMe_3}$; $\mathrm{R=Me}$, Ph, Tol) add electrophilic agents like sulfur, protic acids, methylthio tetrafluoroborate or chlorodimethylphosphine to afford dithiocarboxylates [12, 13], η^2-acyl complexes [14–16], η^2-thiocarbene complexes $[\mathrm{CpL(CO)\overline{W{=}C(R)S}Me}][\mathrm{BF_4}]$ [17–21] and η^3-phosphinoketene complexes [22]. The η^2-thiocarbene complexes show a pronounced amphiphilic reactivity [20, 21] towards Lewis acids and Lewis bases. The related η^2-phosphinocarbene complexes $[\mathrm{CpL(CO)\overline{W{=}C(R)P}R_2}][\mathrm{PF_6}]$ [23], however, have been synthesized via treatment of suitable η^2-ketenyl complexes [24, 25] with halophosphines followed by a chloride–hexafluorophosphate exchange and subsequent decarbonylation of the resulting tungstaphosphabicyclo[1.1.0]butanone hexafluorophosphate [26].

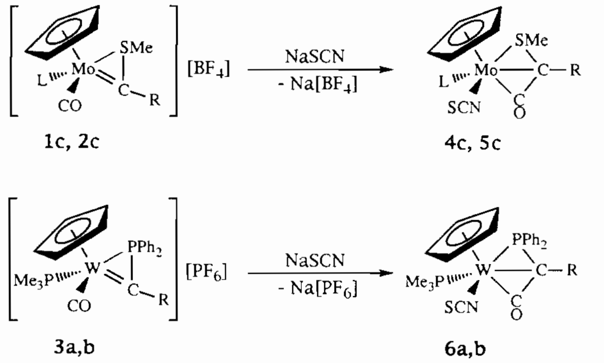
Results and discussion

The addition of sodium thiocyanate to η^2-thiocarbene complexes $[\mathrm{Cp(CO)L\overline{Mo{=}C(Tol){-}S}Me}][\mathrm{BF_4}]$ ($\mathrm{L=}$ CO, $\mathrm{PMe_3}$) (**1c**, **2c**) [19] or η^2-phosphinocarbene complexes $[\mathrm{Cp(CO)(PMe_3)\overline{W{=}C(R){-}P}Ph_2}][\mathrm{PF_6}]$ ($\mathrm{R=Me}$, Ph) (**3a** [23] and **3b**) in $\mathrm{CH_2Cl_2}$ at low temperatures generates via carbonyl carbene coupling molybdathia- (**4c**, **5c**) or tungstaphosphabicyclo[1.1.0]butanone complexes (**6a,b**) in excellent yields (eqn. (1)). In the case of dicarbonyl(η^5-cyclopentadienyl)(η^2-methylthio-tolylcarbene)molybdenum (**1c**) two isomers (**5c**, **5c′** ~ 4:1) are formed. **3b** is prepared by adding chlorodiphenylphosphine to carbonyl-(η^5-cyclopentadienyl)-trimethylphosphine-(η^2-phenylketenyl)tungsten (**8b**) [25] providing tungstaphosphabicyclo[1.1.0]butanone chloride. After a subsequent chloride/hexafluorophosphate exchange stirring at 38 °C causes loss of CO to yield **3b** (eqn. (2)).

---

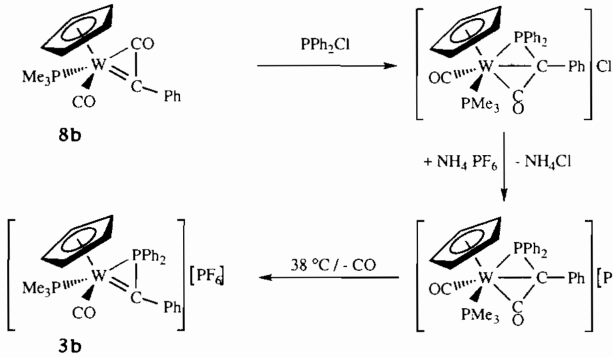
*Author to whom correspondence should be addressed.

0020-1693/94/$07.00
SSDI 0020-1693(94)03896-V



(1)

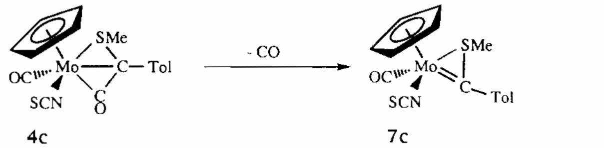
1, 4: L = CO; 2, 5: L = PMe$_3$; a: R = Me; b: R = Ph; c: R = Tol



(2)

The red (**4c**, **5c**) to yellow (**6a,b**), diamagnetic compounds are slightly soluble in dichloromethane and in solution are temperature sensitive. The composition of these compounds was confirmed by elemental analysis, IR, proton, ^{13}C phosphorus NMR spectroscopy as well as FAB (**4c**, **5c**) or FD (**6a,b**) mass spectrometry.

On heating the molybdenum complex **4c** in dichloromethane to 38 °C loss of carbon monoxide takes place to form the neutral η^2-thiocarbene complex of molybdenum (**7c**) (eqn. (3)).



(3)

The IR spectra (Table 1) of the new metallabicyclo[1.1.0]butanone compounds **4c**–**6b** and the neutral η^2-thiocarbene complex **7c** in dichloromethane display in the ν(CO) region the expected vibrations for the carbonyl, the SCN ligands as well as for the bridging carbonyl group.

TABLE 1. IR spectra of **3b**–**7c** in dichloromethane in the ν(CO) region (cm^{-1})

Compound	M–CO	M–SCN	Ring CO
3b	1932vs, 1981s		
4c	2024vs	2081vs	1670m
5c		2077vs	1634m
6a		2078vs	1593m
6b		2079vs	1606m
7c	1967vs	2082vs	

The addition of the SCN unit to the η^2-carbene complexes **1c**–**3b** causes in the ^{1}H NMR spectra (Table 2) of **4c**–**6b** a slight additional shielding of the cyclopentadienyl protons. The conversion of the η^2-carbene into the metallabicyclobutanone complex does not significantly influence the chemical shifts of the remaining protons.

The ^{13}C NMR spectra also agree with the proposed metallabicyclobutanone structure (Table 3) for **4c**–**6b**. Of special interest are the data of both ring carbon atoms as discussed for **6b**. Thus the chemical shift of δ 16.7 ppm can be regarded as a good indication for a remarkable degree of σ-bonding to the metal [27]. The signal splits into a doublet of doublets due to spin–spin interactions ($^1J(^{31}P–^{13}C) = 22.3$, $^2J(^{31}P–^{13}C) = 5.6$ Hz) with both phosphorus atoms. For the related cationic tungstaphosphabicyclo[1.1.0]butanone complexes [26] chemical shifts of δ 2 ppm are reported. Due to insufficient solubility of **6b** the ^{183}W–^{13}C coupling has not been detected up to now. For the ring carbonyl group of **6b** with δ 250.5 ppm the same pattern is observed with $^2J(^{31}P–^{13}C) = 9.1$ Hz and $^2J(^{31}P–^{13}C) = 9.1$ Hz.

The ^{13}C NMR spectrum of the starting carbene complex **3b** shows two doublets of doublets; one for the carbonyl carbon at δ 211 ppm (dd, 30.8, 7.8 Hz) and one for the carbene carbon at δ 206 ppm (dd, 34.9, 8.3 Hz).

The phosphorus NMR spectra (Table 4) of the new cyclic compounds **3b**, **6a** and **6b** display the expected characteristic features of a three-membered metal–phosphorus–carbon cycle with a strong shielding of the ring phosphorus [28, 29] as well as a decrease of the tungsten–phosphorus coupling constants [29, 30] compared to those of monodentate phosphine ligands.

Crystal structure determination

All X-ray investigations were performed on an automated four-circle diffractometer CAD4 (ENRAF-NONIUS, Delft) with graphite-monochromated Mo Kα radiation at low temperature of −71 °C to avoid decomposition of the crystal. A red single crystal of approximate dimensions 0.25×0.25×0.15 mm was sealed in a glass capillary. The lattice parameters were determined by refinement of the diffraction geometry of 25 precisely centered high-angle reflections. Intensity data were collected with ω/θ scan. During the exposure time of 68.7 h no loss of intensity was observed. The W and P positions from inspection of the Patterson

TABLE 2. ^{1}H NMR spectra in CD_2Cl_2 (δ)

	3b	4c	5c	6a	6b	7c
$C_6H_{4/5}$	7.30 (m)	7.33 (m)	7.25 (m)	7.60 (m)	7.38 (m)	7.46 (m)
C_5H_5	5.78 (s)	5.45 (s)	^{i}4.92 (d, 1.9) ^{ii}4.90 (d, 1.9)	4.62 (dd, 2.0; 2.0)	4.69 (s)	5.49 (s)
SCH_3		2.22 (s)	^{i}2.30 (s) ^{ii}2.29 (s)			2.06 (s)
CCH_3		2.35 (s)	^{i}2.33 (s) ^{ii}2.35 (s)	2.12 (s)		2.39 (s)
PCH_3	11.29 (d, 9.8)		^{i}0.99 (d, 10.0) ^{ii}1.09 (d, 10.0)	1.49 (d, 9.3)	1.10 (d, 9.8)	

^{i}Isomer i. ^{ii}Isomer ii.

TABLE 3. $^{13}C\{^{1}H\}$ NMR spectra in CD_2Cl_2 (δ)

	3b	4c	5c	6a	6b
M–CO	210.9 (dd, 30.8; 7.8)^{a}	225.0			
M–C(O)–		251.6	^{i}262.4 (d, 10.1)^{a}, ^{iic}	254.2 (dd, 15.6; 4.6)^{a} (26.2)^{b}	250.5 (dd, 9.1; 9.1)^{a}
$C_6H_{4/5}$	136.3–118.6	137.6–125.3	141.7–126.9	135.8–126.6	136.5–125.9
SCN		145.7	134.7	148.3	148.8
C_5H_5	82.8	94.5	^{i}92.9, ^{ii}92.3	87.1	87.5
M–C–R	205.6 (dd, 34.9; 8.3)^{a}	49.2	^{c}	14.9 (d, 28.5 br)^{a}	16.7 (dd, 22.3; 5.6)^{a}
PMe_3	11.5 (d, 36.7)^{a}		^{i}16.0 (d, 28.0)^{a} ^{ii}16.1 (d, 28.0)^{a}	16.1 (d, 29.4)^{a}	15.2 (d, 30.3)^{a}
C–CH_3		20.9	^{i}21.2, ^{ii}21.4	9.9	
S–CH_3		25.4	^{i}24.8, ^{ii}24.7		

^{a} $^{1}J(^{31}P–^{13}C)$ and/or $^{2}J(^{31}P–^{13}C)$. ^{b} $^{1}J(^{183}W–^{13}C)$. ^{c}Identification not clear. ^{i}Isomer i. ^{ii}Isomer ii.

TABLE 4. $^{31}P\{^{1}H\}$ NMR spectra in CD_2Cl_2 (δ)

	PMe_3	PPh_2	PF_6^-
3b	−26.4 (d, 7.1^{a}, 338.3^{b})	−113.2 (d, 8.5^{a}, 72.1^{b})	146.2 (d, 710.7^{c})
5c	^{i}7.1; ^{ii}6.8		
6a	−20.4 (d, 20.5^{a}, 262.8^{b})	−28.1 (d, 20.5^{a}, 204.8^{b})	
6b	−23.1 (d, 21.2^{a}, 261.4^{b})	−31.7 (d, 21.2^{a}, 200.6^{b})	

$^{a2}J(^{31}P–^{31}P)$. $^{b1}J(^{183}W–^{31}P)$. $^{c1}J(^{19}F–^{31}P)$. ^{i}Isomer i. ^{ii}Isomer ii.

map and subsequent difference-Fourier synthesis revealed the positions of all non-H atoms. After refinement with unique merged data and isotropic displacement factors the procedure for the empirical absorption correction with the program DIFABS [31] was applied. The final full-matrix least-squares refinement (on F^2) with anisotropic displacement parameters for all non-H atoms, and positions of the H atoms in calculated idealized positions, led to R values of $R^1=0.0239$ and $R_w{}^2=0.058$ with $R^1=(\Sigma\|F_o|-|F_c\|)/\Sigma|F_c|$ and $R_w{}^2=[\Sigma(w(F_o{}^2-F_c{}^2)^2/\Sigma(\omega(F_o{}^2)^2)]^{0.5}$. Calculations were performed with the programs CADSHEL, SHELXS-86, SHELXL-93 and the SHELXTL-PLUS package [32]. A summary of the crystal data, data collection and structure refinement parameters is given in Table 5. Final atomic coordinates are listed in Table 6, and selected bond distances and angles in Table 7. A graphic representation of the two symmetry-independent molecules (A and B) is shown in Fig. 1.

The bond distances from tungsten to the cyclopentadienyl, to the trimethylphosphine and to the isothiocyanato ligand are comparable to other tungsten complexes. Within the W–P–C ring the W(1)–P(1) (238.9(1) pm), the W(1)–C(1) (234.1(3) pm) and the P(1)–C(1) (175.3(3) pm) bond distances are similar to those reported for three-membered metallaphospha-

TABLE 5. Crystal data for compound **6b**

Empirical formula	$C_{29}H_{29}NOP_2SW \cdot CH_2Cl_2$
Formula weight (g/mol)	770.31
Temperature (K)	202(2)
Wavelength (Å)	0.71073
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	10.547(1)
b (Å)	18.531(2)
c (Å)	18.710(2)
α (°)	118.84(1)
β (°)	95.40(1)
γ (°)	102.09(1)
Volume (Å^3)	3049.8(5)
Formula units	4
Density (calc) (g/cm^3)	1.678
Absorption coefficient (mm^{-1})	4.161
F(000)	1520
θ Range for data collection (°)	2.03–26.96
Index ranges	$-13 \leqslant h \leqslant 13$, $0 \leqslant k \leqslant 23$, $-23 \leqslant l \leqslant 20$
Reflections collected	13250
Reflections unique	13249
Reflections observed	11509 ($F_o > 4\sigma(F_o)$)
Refinement method	full-matrix least-squares on F^2
No. variables	691
Goodness-of-fit on F^2	1.040
Final R indices ($I > 4\sigma(I)$)	
R^1	0.0239
$R_w{}^2$	0.0580
R indices (all data)	
R^1	0.0321
$R_w{}^2$	0.0619
Residual electron density, ρ max., min. (e Å)	0.953, −0.989

heterocycles [33, 34] or to the metallaphosphabicyclo[1.1.0]butanone complex [Cp(CO)(PMe$_3$)W–η^3-P(Me$_2$)–C(Me)–C(O)]Cl [26].

Compared to the last one the bridging carbonyl group shows a slight slippage towards the metal. See also 'Supplementary material'.

The reaction of sodium thiocyanate with the cationic η^2-thiocarbene complexes [Cp(CO)LMo=C(Tol)–SMe][BF$_4$] (**1c**, **2c**) or η^2-phosphinocarbene complexes [Cp(CO)(PMe$_3$)W=C(R)–PPh$_2$][PF$_6$] (**3a,b**) results in a coordination of the SCN$^-$ anion as an isothiocyanato and not as a thiocyanato ligand. Thus, in the cationic η^2-carbene complex tungsten behaves like a borderline metal in agreement with the periodic table of Ahrland *et al.* [35] according to which metal ions in their common oxidation states can be divided roughly into two groups, depending on the abilities to coordinate donor atoms.

The possible electrophilic attack of the thiocyanate anion at the metal coordinated carbene carbon could not be excluded a priori. Thus, ammonia, primary or uncrowded secondary amines [36, 37], rigid tertiary amines such as 1-azabicyclo[2.2.2]octane or 1,4-diazabicyclo[2.2.2]octane [37, 38], secondary or tertiary phosphines [37, 39, 40], thiols [37, 41] and selenols [37, 42] attack in a typical reaction the carbene carbon in most of the Fischer carbene complexes with chromium, molybdenum, tungsten, manganese or rhenium using a variety of carbene ligands as well as in selected cationic η^2-thio- [43, 44] or η^2-phosphinocarbene complexes [45].

The metal induced carbon–carbon coupling reaction is well known for distinct transition metal carbene as well as carbyne complexes. Thus nickel tetracarbonyl reacts with diazomethane via an intermediate nickel carbene complex to yield a free ketene [46]. The same type of coupling is reported on the high pressure carbonylation of dicarbonyl(η^5-cyclopentadienyl)diphenylcarbene manganese [47] or the thermal decomposition of pentacarbonyl(diphenylcarbene)tungsten [48]. For transition metal carbyne complexes like Cp(CO)$_2$M≡CR the nucleophilic carbonyl carbyne coupling is well investigated [11, 24, 49]. Subsequently the application of the nucleophilic or electrophilic induced carbonyl carbyne coupling reaction has been perfectly demonstrated by Fischer *et al.* [50, 51], Schrock and co-workers [52], Templeton and co-workers [53, 54],

TABLE 6. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **6b**

	x/a	y/b	z/c	U_{eq}[a]
Molecule A				
W(1)	2520(1)	7202(1)	3669(1)	36(1)
P(1)	2896(1)	6241(1)	2342(1)	37(1)
P(2)	2367(1)	8711(1)	4334(1)	41(1)
S(1)	7346(1)	8519(1)	4537(1)	58(1)
N(1)	4581(3)	7854(2)	4013(2)	40(1)
O(1)	−12(2)	7010(2)	2488(2)	52(1)
C(1)	2312(3)	7062(2)	2348(2)	39(1)
C(2)	1135(3)	7023(2)	2703(2)	41(1)
C(3)	5733(3)	8145(2)	4238(2)	41(1)
C(4)	2321(4)	6133(2)	3996(2)	53(1)
C(5)	1050(4)	6098(2)	3609(2)	53(1)
C(6)	776(4)	6882(2)	4164(2)	52(1)
C(7)	1857(4)	7373(2)	4882(2)	50(1)
C(8)	2795(4)	6908(2)	4762(2)	51(1)
C(11)	2768(3)	7633(2)	2020(2)	42(1)
C(12)	4117(4)	8065(2)	2175(2)	48(1)
C(13)	4482(4)	8657(3)	1924(3)	58(1)
C(14)	3513(5)	8821(3)	1518(3)	66(1)
C(15)	2197(5)	8385(3)	1339(2)	60(1)
C(16)	1825(4)	7787(2)	1585(2)	50(1)
C(21)	4436(3)	6195(2)	1993(2)	38(1)
C(22)	5592(3)	6366(2)	2539(2)	44(1)
C(23)	6783(3)	6358(2)	2279(2)	52(1)
C(24)	6809(4)	6171(2)	1472(3)	55(1)
C(25)	5658(4)	5986(2)	917(2)	53(1)
C(26)	4470(4)	5996(2)	1179(2)	47(1)
C(31)	1707(3)	5188(2)	1648(2)	40(1)
C(32)	1864(3)	4491(2)	1715(2)	43(1)
C(33)	947(4)	3686(2)	1221(2)	47(1)
C(34)	−128(4)	3570(2)	655(2)	55(1)
C(35)	−297(4)	4250(3)	585(2)	56(1)
C(36)	614(3)	5067(2)	1078(2)	48(1)
C(41)	3525(4)	9483(2)	5332(2)	51(1)
C(42)	2664(4)	9242(2)	3743(2)	51(1)
C(43)	761(4)	8834(3)	4557(3)	57(1)
W(2)	−4603(1)	2897(1)	1335(1)	35(1)
P(21)	−3329(1)	3769(1)	2753(1)	37(1)
P(22)	−6247(1)	1421(1)	545(1)	40(1)
S(2)	−1233(1)	1368(1)	680(1)	55(1)
N(2)	−3233(3)	2171(2)	1107(2)	40(1)
O(2)	−6907(2)	3132(2)	2314(2)	55(1)
C(201)	−4705(3)	2931(2)	2582(2)	39(1)
C(202)	−5809(3)	3073(2)	2172(2)	41(1)
C(203)	−2410(3)	1825(2)	921(2)	41(1)
C(204)	−3658(4)	3981(2)	1096(2)	50(1)
C(205)	−4900(4)	4061(2)	1340(2)	48(1)
C(206)	−5918(4)	3333(2)	704(2)	46(1)
C(207)	−5314(4)	2809(2)	69(2)	47(1)
C(208)	−3943(4)	3215(2)	317(2)	48(1)
C(211)	−4791(3)	2313(2)	2873(2)	42(1)
C(212)	−3860(3)	1857(2)	2800(2)	46(1)
C(213)	−4058(4)	1226(3)	3007(2)	56(1)
C(214)	−5165(4)	1044(3)	3298(3)	62(1)
C(215)	−6060(4)	1514(3)	3410(2)	58(1)
C(216)	−5876(4)	2150(2)	3206(2)	49(1)
C(221)	−1736(3)	3763(2)	3200(2)	39(1)
C(222)	−747(3)	3646(2)	2751(2)	46(1)
C(223)	496(4)	3672(3)	3111(3)	54(1)
Molecule A				
C(224)	732(4)	3811(3)	3910(3)	57(1)
C(225)	−242(4)	3929(3)	4361(2)	53(1)
C(226)	−1476(4)	3908(2)	4009(2)	47(1)
C(231)	−3508(3)	4803(2)	3514(2)	40(1)
C(232)	−4566(4)	4858(2)	3908(2)	50(1)
C(233)	−4663(4)	5664(3)	4491(2)	55(1)
C(234)	−3743(4)	6398(2)	4669(2)	52(1)
C(235)	−2697(4)	6350(2)	4279(3)	55(1)
C(236)	−2572(3)	5555(2)	3705(2)	49(1)
C(241)	−6029(5)	673(3)	−476(3)	71(1)
C(242)	−6291(5)	791(3)	1039(3)	67(1)
C(243)	−7977(4)	1385(3)	336(3)	66(1)
Solvent CH_2Cl_2				
C(50)	8439(9)	8422(4)	2481(4)	124(3)
Cl(51)	8758(4)	9446(2)	3122(2)	209(2)
Cl(52)	8395(2)	8076(1)	1409(1)	110(1)
C(60)	129(1)	1377(6)	2523(4)	149(4)
Cl(61)	338(2)	1643(1)	3550(1)	118(1)
Cl(62)	494(2)	438(1)	1852(1)	105(1)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

James and Stone [55], Angelici and co-workers [56, 57], Mayr *et al.* [58, 59], Geoffroy and co-workers [60] and Lippard and co-workers [61], preparing a variety of interesting ketenyl, alkyne and binuclear complexes involving η^2-ketenyl species as possible intermediates.

Experimental

Preparation of carbonyl-(η^5-cyclopentadienyl)-(trimethylphosphine)-[η^2-(diphenylphosphino)-phenylcarbene]tungsten (3b)

At −78 °C 3.3 ml (1.8 mmol) chlorodiphenylphosphine were added to a solution of 0.88 g (1.81 mmol) carbonyl-(η^5-cyclopentadienyl)-trimethylphosphine-(η^2-phenylketenyl)tungsten (**8b**) in 30 ml of dichloromethane. After stirring for ½ h at this temperature 2.9 g (18.0 mmol) of ammoniumhexafluorophosphate were added to the formed but not isolated tungstaphosphabicyclo[1.1.0]butanone chloride to exchange the chloride by the hexafluorophosphate anion. After 24 h stirring at −40 °C the resulting tungstaphosphabicyclo-[1.1.0]butanone hexafluorophosphate was precipitated by adding pentane. Subsequent treatment of a dichloromethane solution of this intermediate product at 38 °C for 2 h causes loss of CO to yield **3b**. Further purification by recrystallization with dichloromethane/pentane and drying under vacuum yielded 1.2 g (86%) of **3b**, violet crystals. MS (FD in CH_2Cl_2): *m/z* 627 $(M)^+$, *m/z* 599 $(M-CO)^+$. *Anal.* Calc. for

TABLE 7. Selected bond lengths (Å) and angles (°) for **6b**

W(1)-P(1)	2.389(1)	W(2)-P(21)	2.395(1)
W(1)-P(2)	2.504(1)	W(2)-P(22)	2.511(1)
W(1)-N(1)	2.118(3)	W(2)-N(2)	2.111(3)
W(1)-C(1)	2.341(3)	W(2)-C(201)	2.316(3)
W(1)-C(2)	2.058(3)	W(2)-C(202)	2.057(3)
W(1)-C(4)	2.316(4)	W(2)-C(204)	2.311(3)
W(1)-C(5)	2.241(3)	W(2)-C(205)	2.239(3)
W(1)-C(6)	2.234(3)	W(2)-C(206)	2.249(3)
W(1)-C(7)	2.333(3)	W(2)-C(207)	2.334(3)
W(1)-C(8)	2.365(3)	W(2)-C(208)	2.372(3)
P(1)-C(1)	1.753(3)	P(21)-C(201)	1.763(3)
P(1)-C(21)	1.810(3)	P(21)-C(221)	1.809(3)
P(1)-C(31)	1.814(3)	P(21)-C(231)	1.819(3)
S(1)-C(3)	1.626(3)	S(2)-C(203)	1.624(3)
N(1)-C(3)	1.163(4)	N(2)-C(203)	1.166(4)
O(1)-C(2)	1.231(4)	O(2)-C(202)	1.228(4)
C(1)-C(2)	1.467(4)	C(201)-C(202)	1.472(4)
P(1)-W(1)-P(2)	133.18(3)	P(21)-W(2)-P(22)	132.21(3)
P(1)-W(1)-N(1)	86.54(8)	P(21)-W(2)-N(2)	86.92(8)
P(1)-W(1)-C(1)	43.49(8)	P(21)-W(2)-C(201)	43.92(8)
P(1)-W(1)-C(2)	69.04(9)	P(21)-W(2)-C(202)	68.68(9)
P(2)-W(1)-N(1)	81.79(7)	P(22)-W(2)-N(2)	81.82(8)
P(2)-W(1)-C(1)	91.63(8)	P(22)-W(2)-C(201)	89.82(8)
P(2)-W(1)-C(2)	82.35(9)	P(22)-W(2)-C(202)	81.45(9)
N(1)-W(1)-C(1)	91.94(11)	N(2)-W(2)-C(201)	90.95(11)
N(1)-W(1)-C(2)	126.71(12)	N(2)-W(2)-C(202)	126.50(12)
C(1)-W(1)-C(2)	38.27(11)	C(201)-W(2)-C(202)	38.78(11)
W(1)-P(1)-C(1)	66.8(1)	W(2)-P(21)-C(201)	65.7(1)
W(1)-P(1)-C(21)	129.8(1)	W(2)-P(21)-C(221)	129.0(1)
W(1)-P(1)-C(31)	120.5(1)	W(2)-P(21)-C(231)	124.2(1)
C(1)-P(1)-C(21)	112.7(2)	C(201)-P(21)-C(221)	115.2(2)
C(1)-P(1)-C(31)	111.7(2)	C(201)-P(21)-C(231)	109.8(2)
C(21)-P(1)-C(31)	106.4(2)	C(221)-P(21)-C(231)	104.1(2)
W(1)-N(1)-C(3)	171.5(3)	W(2)-N(2)-C(203)	170.5(3)
W(1)-C(1)-P(1)	69.7(1)	W(2)-C(201)-P(21)	70.4(1)
W(1)-C(1)-C(2)	60.3(2)	W(2)-C(201)-C(202)	61.1(2)
W(1)-C(1)-C(11)	136.0(2)	W(2)-C(201)-C(211)	136.5(2)
P(1)-C(1)-C(2)	103.5(2)	P(21)-C(201)-C(202)	102.3(2)
P(1)-C(1)-C(11)	130.9(2)	P(21)-C(201)-C(211)	129.6(2)
C(2)-C(1)-C(11)	125.4(3)	C(202)-C(201)-C(211)	127.6(3)
W(1)-C(2)-O(1)	144.7(3)	W(2)-C(202)-O(2)	146.7(3)
W(1)-C(2)-C(1)	81.4(2)	W(2)-C(202)-C(201)	80.2(2)
O(1)-C(2)-C(1)	133.1(3)	O(2)-C(202)-C(201)	132.3(3)
S(1)-C(3)-N(1)	178.1(3)	N(2)-C(203)-S(2)	178.5(3)

$C_{28}H_{29}WP_3OF_6$: C, 43.50; H, 3.78; W, 23.80. Found: C, 43.34; H, 3.75; W, 23.81%.

Preparation of 1-carbonyl-1-cyclopentadienyl-1-isothiocyanato-2-methyl-3-(4-methylphenyl)-1-molybda-2-thia-bicyclo[1.1.0]butan-4-one (4c)

At −40 °C to a solution of 0.38 g (8.4 mmol) **1c** in 30 ml of dichloromethane 2.04 g (25.2 mmol) sodium thiocyanate were added. After stirring for 14 h at this temperature, the dark red mixture was filtered through a fine-porosity frit and precipitated with dichloromethane/pentane at −78 °C. Recrystallization with dichloromethane/pentane and drying under vacuum at −40 °C yielded 0.33 g (93%) of **3c**, a red powder. MS (FAB in nitrobenzylalcohol): *m/z* 369 $(M-SCN)^+$. *Anal.* Calc. for $MoC_{17}H_{15}O_2S_2N \cdot 0.5CH_2Cl_2$: C, 46.39; H, 3.49; N, 3.13; Mo, 21.48. Found: C, 46.31; H, 3.5; N, 3.23; Mo 20.86%.

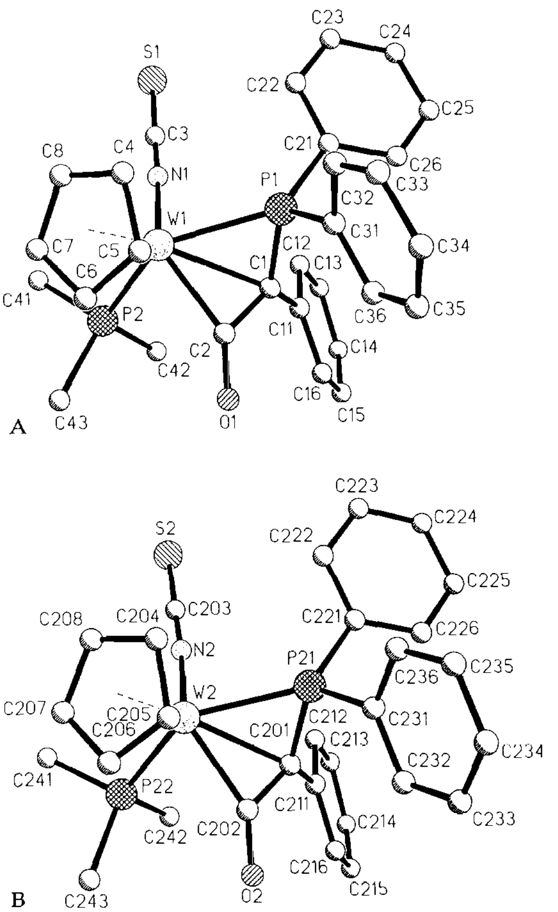


Fig. 1. Plot of the two symmetry independent molecules of **6b** (A and B) along with the atom numbering scheme.

Preparation of 1-cyclopentadienyl-1-isothiocyanato-1-trimethylphosphine-2-methyl-3-(4-methylphenyl)-1-molybda-2-thia-bicyclo[1.1.0]butan-4-one (4c)

In an analogous procedure to a solution of 0.05 g (0.1 mmol) **2c** in 25 ml of dichloromethane was added at −25 °C 0.04 g (0.5 mmol) sodium thiocyanate. After stirring for 5 h at this temperature, the light red mixture was filtered and purified as described above. Yield 0.025 g (54%) of **4c**, a pale pink powder. MS (FAB in nitrobenzylalcohol): *m/z* 475 $(M)^+$, *m/z* 447 $(M-CO)^+$, *m/z* 419 $(M-SCN)^+$. *Anal.* Calc. for $MoC_{19}H_{24}S_2OPN$: C, 48.2; H, 5.11; N, 2.96. Found: C, 47.85; H, 5.03; N, 2.89%.

Preparation of 1-cyclopentadienyl-1-isothiocyanato-1-trimethylphosphine-2,2-diphenyl-3-methyl-1-tungsta-2-phospha-bicyclo[1.1.0]butan-4-one (6a)

At room temperature 0.5 g (6.17 mmol) of sodium thiocyanate was added to 0.26 g (0.37 mmol) of **3a** in approximately 20 ml of dichloromethane. After 12 h stirring the solution was filtered and the product was precipitated with ether/pentane. Recrystallization with dichloromethane/pentane and drying under high vacuum yielded 0.21 g (92%) of **6a**, a deep yellow powder. MS (FD in CH_2Cl_2): m/z 565 $(M-SCN)^+$, m/z 405 $(M-PMe_3-Ph-C_5H_5)^+$. *Anal.* Calc. for $C_{24}H_{27}WP_2NSO$: C, 46.24; H, 4.37; N, 2.25. Found: C, 45.9; H, 4.2; N, 2.0%.

Preparation of 1-cyclopentadienyl-1-isothiocyanato-1-trimethylphosphine-2,2,3-triphenyl-1-tungsta-2-phospha-bicyclo[1.1.6]butan-4-one (6b)

In an analogous procedure 0.4 g (4.94 mmol) of sodium thiocyanate was added to 0.27 g (0.35 mmol) of **3b** in 30 ml of dichloromethane. The likewise isolation yielded 0.2 g (83%) of **6b**, a pale yellow powder, MS (FD in CH_2Cl_2): m/z 657 $(M-CO)^+$, m/z 627 $(M-SCN)^+$. *Anal.* Calc. for $C_{29}H_{29}WP_2NSO \cdot 0.9CH_2Cl_2$: C, 47.14; H, 4.08; N, 1.83. Found: C, 47.21; H, 4.47; N, 1.75%. This route provided the crystal for X-ray analysis (see above).

Preparation of carbonyl-(η^5-cyclopentadienyl)-(isothiocyanato)[η^2-(methylthio)(4-methylphenyl)-carbene]molybdenum (7c)

At 25 °C to a solution of 0.5 g (1.1 mmol) **1c** in 50 ml dichloromethane 0.44 g (5.5 mmol) sodium thiocyanate was added. After stirring at 38 °C for 3 h the dark green solution was filtered through a fine-porosity frit. Purification by column chromatography on Merck silica gel (dichloromethane/pentane = 1:1, −40 °C) yielded a green oil. Further purification by recrystallization with dichloromethane/pentane and drying under vacuum at −20 °C yielded 0.11 g (24%) of **7c**, a green powder. MS (FAB in nitrobenzylalcohol): m/z 399 $(M)^+$, m/z 371 $(M-CO)^+$, m/z 341 $(M-SCN)^+$. *Anal.* Calc. for $MoC_{16}H_{15}S_2ON$: C, 49.6; H, 4.21; N, 2.96. Found: C, 49.1; H, 4.13, N, 2.88%.

Supplementary material

Further details of the X-ray structure analysis are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-58114, the names of the authors, and the journal citation.

Acknowledgements

This work has been supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We thank Mrs R. Dumitrescu for the MS investigations, Mr J. Riede for the X-ray measurements, and Mr M. Barth for the elemental analysis.

References

1 E.O. Fischer and A. Maasböl, *Angew. Chem., 76* (1964) 645; *Angew. Chem., Int. Ed. Engl., 3* (1964) 580.

2 E.O. Fischer, G. Kreis, C.G. Kreiter, J. Müller, G. Huttner and H. Lorenz, *Angew. Chem., 85* (1973) 618; *Angew. Chem., Int. Ed. Engl., 12* (1973) 564.

3 K.H. Dötz, H. Fischer, P. Hofmann, F.R. Kreißl, U. Schubert and K. Weiss (eds.), *Transition Metal Carbene Complexes,* Verlag Chemie, Weinheim, Germany, 1983.

4 (a) H.P. Kim and R.J. Angelici, *Adv. Organomet. Chem., 27* (1987) 51; (b) H. Fischer, P. Hofmann, F.R. Kreißl, R.R. Schrock, U. Schubert and K. Weiss (eds.), *Carbyne Complexes,* VCH, Weinheim, Germany, 1988.

5 F.R. Kreißl (ed.), *Transition Metal Carbyne Compelxes,* Kluwer, Dordrecht, Netherlands, 1993.

6 N.M. Kostic and R.F. Fcnskc, *J. Am. Chem. Soc., 103* (1981) 4677.

7 R.F. Fenske, in *Organometallic Compounds: Synthesis, Structure and Theory,* Texas A&M University Press, College Station, TX, 1983, p. 305.

8 P Hofmann, in *Transition Metal Carbene Complexes,* Verlag Chemie, Weinheim, Germany, 1983, p. 113.

9 E.O. Fischer, T.L. Lindner and F.R. Kreißl, *J. Organomet. Chem., 112* (1976) C27.

10 E.O. Fischer, T.L. Lindner, G. Huttner, P. Friedrich, F.R. Kreißl and J.O. Besenhard, *Chem. Ber., 110* (1977) 3397.

11 W. Uedelhoven, K. Eberl and F.R. Kreißl, *Chem. Ber., 112* (1979) 3376.

12 D.S. Gill, M. Green, K. Marsden, I. Moore, A.G. Orpen, F.G.A. Stone, I.D. Williams and P. Woodward, *J. Chem. Soc., Dalton Trans.,* (1984) 1343.

13 F.R. Kreißl and N. Ullrich, *J. Organomet. Chem., 361* (1989) C30.

14 F.R. Kreißl, W.J. Sieber, M. Wolfgruber and J. Riede, *Angew. Chem., 96* (1984) 618; *Angew. Chem., Int. Ed. Engl., 23* (1984) 640.

15 F.R. Kreißl, W.J. Sieber, H. Keller, J. Riede and M. Wolfgruber, *J. Organomet. Chem., 320* (1987) 83.

16 F.R. Kreißl, H. Keller and W. Schütt, *J. Organomet. Chem., 441* (1992) 75.

17 F.R. Kreißl and H. Keller, *Angew. Chem., 89* (1986) 924; *Angew. Chem., Int. Ed. Engl., 25* (1986) 904.

18 W. Schütt, N. Ullrich and F.R. Kreißl, *J. Organomet. Chem., 408* (1991) C5.

19 N. Ullrich, C.M. Stegmair, H. Keller, E. Herdtweck and F.R. Kreißl, *Z. Naturforsch., Teil B, 45* (1990) 921.

20 F.R. Kreißl and C.M. Steigmair, *Chem. Ber., 124* (1991) 2747.

21 F.R. Kreißl, W. Schütt, C.M. Stegmair, N. Ullrich, H. Keller, J. Ostermeier and E. Herdtweck, *Chem. Ber., 126* (1993) 1609.

22 M. Wolfgruber, C.M. Stegmair and F.R. Kreißl, *J. Organomet. Chem., 376* (1989) 45.

23 F.R. Kreißl, M. Wolfgruber and W.J. Sieber, *J. Organomet. Chem., 270* (1984) C4.

24 F.R. Kreißl, P. Friedrich and G. Huttner, *Angew. Chem., 89* (1977) 110; *Angew. Chem., Int. Ed. Engl., 16* (1977) 102.

25 F.R. Kreißl, K. Eberl and W. Uedelhoven, *Chem. Ber., 110* (1977) 3782.

26 F.R. Kreißl, M. Wolfgruber, W.J. Sieber and K. Ackermann, *Organometallics, 3* (1984) 777.

27 F.H. Köhler, H.J. Kalder and E.O. Fischer, *J. Organomet. Chem., 85* (1975) C19.

28 H. Schmidbaur and E. Blaschke, *Z. Naturforsch., Teil B, 35* (1980) 584.

29 P.E. Garrou, *Chem. Rev., 81* (1981) 229.

30 S. Bresandola, E. Longato and F.J. Morandini, *J. Organomet. Chem., 128* (1977) C5.

31 (a) N. Walker and D. Stuart, *Acta Crystallogr., Sect. A, 39* (1983) 158; (b) N. Walker, *Program DIFABS*, Version 9.0, BASF AG, 1993.

32 (a) J. Kopf and H-Chr. Rübcke, *Program CADSHEL,* Version 3.1, University of Hamburg, Germany, 1993; (b) G.M. Sheldrick, Program SHELXS-86, University of Göttingen, Germany; G.M. Sheldrick, C. Krüger and R. Goddard (eds.), *Crystallographic Computing 3,* Oxford University Press, Oxford, 1985, pp. 175–189; (c) G.M. Sheldrick, *Program SHELXL-93,* University of Göttingen, Germany; *J. Appl. Crystallogr.,* in press; (d) *Program Package SHELXTL-PLUS*, Release 4.1, 1990 Siemens Analytical X-Ray Instruments, Inc., Madison, WI, USA, 1990.

33 F.A. Cotton, L.R. Falvello and R.C. Najjar, *Organometallics, 1* (1982) 1640.

34 N. Bresciani-Pahor, M. Caligaris, P. Delise, G. Nardin and L. Randaccio, *J. Am. Chem. Soc., 96* (1974) 5642.

35 S. Ahrland, J. Chatt and N.R. Davis, *Q. Rev., 11* (1958) 265.

36 U. Klabunde and E.O. Fischer, *J. Chem. Soc. A,* (1969) 578.

37 F.R. Kreißl, in K.H. Dötz, H. Fischer, P. Hofmann, F.R. Kreißl, U. Schubert and K. Weiss (eds.), *Transition Metal Carbene Complexes,* Verlag Chemie, Weinheim, Germany, 1983, p. 151.

38 F.R. Kreißl, E.O. Fischer, C.G. Kreiter and K. Weiß, *Angew. Chem., 85* (1977) 617; *Angew. Chem., Int. Ed. Engl., 12* (1973) 563.

39 F.R. Kreißl, C.G. Kreiter and E.O. Fischer, *Angew. Chem., 84* (1972) 679; *Angew. Chem., Int. Ed. Engl., 11* (1972) 643.

40 F.R. Kreißl, E.O. Fischer, C.G. Kreiter and H. Fischer, *Chem. Ber., 106* (1973) 1262.

41 E.O. Fischer, M. Leupold, C.G. Kreiter and J. Müller, *Chem. Ber., 105* (1972) 150.

42 E.O. Fischer, G. Kreis, F.R. Kreißl, C.G. Kreiter and J. Müller, *Chem. Ber., 106* (1973) 3910.

43 H.P. Kim, S. Kim, R.A. Jacobsen and R.J. Angelici, *Organometallics, 5* (1986) 2489.

44 F.R. Kreißl and C.M. Stegmair, *Chem. Ber., 124* (1991) 2747.

45 W. Schütt, E. Herdtweck, F. Hahn and F.R. Kreißl, *J. Organomet. Chem., 443* (1993) C33.

46 Ch. Rüchardt and G.N. Schrauzer, *Chem. Ber., 93* (1960) 1840.

47 W.A. Herrmann, B. Reiter and H. Biersack, *J. Organomet. Chem., 97* (1975) 245.

48 H. Fischer, *Angew. Chem., 95* (1983) 913; *Angew. Chem., Int. Ed. Engl., 22* (1983) 874.

49 F.R. Kreißl, A. Frank, U. Schubert, T.L. Lindner and G. Huttner, *Angew. Chem., 88* (1976) 649; *Angew. Chem., Int. Ed. Engl., 15* (1976) 632.

50 E.O. Fischer and P. Friedrich, *Angew. Chem., 91* (1979) 345; *Angew. Chem., Int. Ed. Engl., 18* (1979) 327.

51 E.O. Fischer, A.C. Filippou, H.G. Alt and K. Ackermann, *J. Organomet. Chem., 254* (1983) C21.

52 S.J. Holmes, R.R. Schrock, M.R. Churchill and H.J. Wasserman, *Organometallics, 3* (1984) 476.

53 K.R. Birdwhistell, T.L. Tonker and J.L. Templeton, *J. Am. Chem. Soc., 107* (1985) 4474.

54 A.S. Gambale, K.R. Birdwhistell and J.L. Templeton, *J. Am. Chem. Soc., 112* (1990) 1818.

55 A.P. James and F.G.A. Stone, *J. Organomet. Chem., 310* (1986) 47.

56 H.P. Kim, S. Kim, R.A. Jacobsen and R.J. Angelici, *Organometallics, 5* (1986) 2481.

57 R.A. Doyle and R.J. Angelici, *Organometallics, 8* (1989) 2207.

58 A. Mayr, G.A. McDermott, A.M. Dorries, A.K. Holder, W.C. Fultz and A.L. Rheingold, *J. Am. Chem. Soc., 108* (1986) 310.

59 A. Mayr, G.A. McDermott, A.M. Dorries and D. Van Engen, *Organometallics, 6* (1987) 1503.

60 J.B. Sheridan, G.L. Geoffroy and A.L. Rheingold, *Organometallics, 5* (1986) 1514.

61 R.N. Vrtis, S. Liu, Ch. P. Rao, S.G. Bott and S.J. Lippard, *Organometallics, 10* (1991) 275.