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Reactions of phosphine-substituted alkylidyne carbonyltungsten complexes with dithiocarbamate ligands: phosphine substitution and alkylidyne–carbonyl coupling

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Abstract

Reaction of the alkylidyne tungsten complexes *cis*- and *trans*- $[W(CPh)Cl(CO)_2(PMe_3)_2]$ with sodium diethyldithiocarbamate affords the ketenyl complex $[W(OCCPh)(S_2CNEt_2)(CO)(PMe_3)_2]$. Reaction of $[W(CPh)Cl(CO)(PMe_3)_3]$ with diethyldithiocarbamate gives the dithiocarbamate-substituted alkylidyne tungsten complex $[W(CPh)(S_2CNEt_2)(CO)(PMe_3)_2]$. Reaction of *cis*-$[W(CPh)Cl(CO)_2(PPh_3)_2]$ with sodium dimethyldithiocarbamate leads to substitution of PPh_3 and formation of $[W(CPh)(S_2CNMe_2)(CO)_2(PPh_3)]$. The solid state structure of $[W(CPh)(S_2CNEt_2)(CO)(PMe_3)_2]$ was determined by X-ray crystallography. Reaction of $[W(CPh)(S_2CNEt_2)(CO)(PMe_3)_2]$ with carbon monoxide in solution as well as in the solid state affords $[W(OCCPh)(S_2CNEt_2)(CO)(PMe_3)_2]$. Pyrolysis of $[W(OCCPh)(S_2CNEt_2)(CO)(PMe_3)_2]$ at 100°C in toluene solution gives $[W(CPh)(S_2CNEt_2)(CO)(PMe_3)_2]$.

Key words: Tungsten; Alkylidyne complexes; Phosphines; Coupling reactions; Ketenyl

1. Introduction

Schrock-type, or high-valent, alkylidyne complexes possess empty low-lying metal d orbitals [1]. Consequently, they are generally stabilized by the presence of strong π donor ligands [2]. In contrast, Fischer-type, or low-valent, alkylidyne complexes do not feature such orbitals [1]. Not surprisingly, very little is known about Fischer-type alkylidyne complexes containing strong π donor ligands [3]. Yet such compounds could be of considerable interest, since the presence of π donor ligands might enhance their reactivity. This paper describes the reactions of some low-valent phosphine-substituted tungsten alkylidyne complexes with dithiocarbamate π donor ligands. Depending on the systems, these reactions lead to the formation of ketenyl tungsten complexes by alkylidyne–carbonyl coupling or to the formation of dithiocarbamate-substituted alkylidyne complexes by phosphine substitution.

2. Results and discussion

cis-$[W(CPh)Cl(CO)_2(PMe_3)_2]$ (***cis-1***) [4] reacts with sodium diethyldithiocarbamate to give the ketenyl complex $[W(OCCPh)(S_2CNEt_2)(CO)(PMe_3)_2]$ (**2**) (eqn. 1). When *trans*-$[W(CPh)Cl(CO)_2(PMe_3)_2]$ (***trans-1***) obtained from ***cis-1*** by photochemical *cis-trans* isomerization [5] is used as the starting material, the same product is obtained (eqn. 1). Complex ***cis-1*** does not transform into ***trans-1*** thermally on the timescale of the reactions shown in eqn. (1). The IR spectrum of **2** exhibits a strong absorption at 1871 cm^{-1} for the carbonyl ligand and an absorption of medium intensity at

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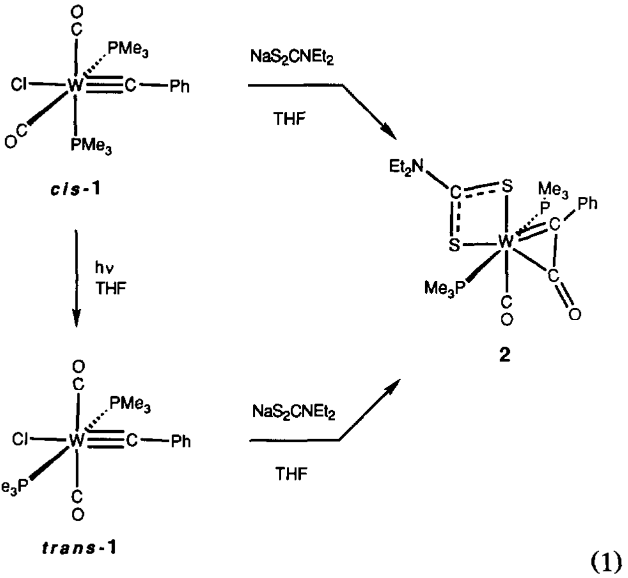
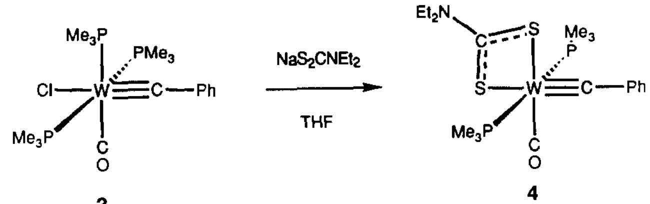
1686 cm^{-1} for the ketenyl ligand. The presence of the ketenyl ligand is confirmed by ^{13}C NMR [6]. The signal for the phenyl-substituted ketenyl carbon atom appears at δ 202.9 ppm as a triplet (J_{PC} = 8.2 Hz). Signals at δ 205.1 and 206.7 ppm are due to the carbon atoms of the ketenyl carbonyl group, PhC*C*O, and the dithiocarbamate ligand, Et_2NCS_2.

Formation of the same product from ***cis-1*** and ***trans-1*** was not expected. It was previously found that the *cis*- and *trans*-isomers of **1** react differently. For example, ***cis-1*** does not react with pyridine (***cis-1*** is prepared from *cis*-[W(CPh)Cl(CO)$_2$(py)$_2$] and PMe$_3$) [4] but ***trans-1*** reacts to give the carbonyl substitution product *trans*-[W(CPh)Cl(CO)(py)(PMe$_3$)$_2$] [5]. A possible outcome of the reaction of ***trans-1*** with dithiocarbamate therefore might have been substitution of the chloride ligand and of one carbonyl ligand to afford [W(CPh)(S$_2$CNEt$_2$)(CO)(PMe$_3$)$_2$] (**4**). Instead, alkylidyne–carbonyl coupling was observed. The effectiveness of dithiocarbamate ligands to induce alkylidyne–carbonyl coupling had previously been demonstrated in the synthesis of the ketenyl complexes [W(OCCCH$_2$-Ph)(S$_2$CNEt$_2$)(CO)(dppe)] [7] (dppe = bis-diphenylphosphinoethane) and [NEt$_4$][M(OCCR)(S$_2$CNEt$_2$)$_2$-(CO)] [8] (M = Mo, W; R = Me, Ph) from [W-(CCH$_2$Ph)(CO)$_2$(dppe)](BF$_4$) and [M(CR)Cl(CO)$_2$-(py)$_2$], respectively, and dithiocarbamate.



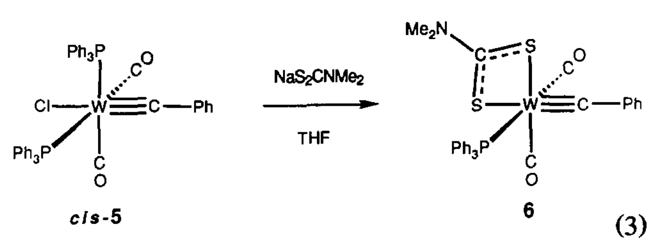
(1)

The synthesis of complex **4** was, however, achieved by reaction of [W(CPh)Cl(CO)(PMe$_3$)$_3$] (**3**) [9] with sodium diethyldithiocarbamate (eqn. 2). The presence of the alkylidyne ligand in **4** is confirmed by the presence of a ^{13}C NMR resonance at δ 271.2 (t, J_{PC} = 11.78 Hz) which exhibits ^{183}W satellites with a characteristically large coupling constant of J_{WC} = 197.5 Hz [4]. The replacement of the chloride and one trimethylphosphine ligand in **3** by dithiocarbamate causes a significant shift of the carbonyl IR absorption from 1896 to 1848 cm^{-1} in **4**. The NMR signal of the carbonyl carbon atom also reflects stronger π backbonding from the metal center in **4** (**3**: δ 227.5 (J_{WC} = 154.4 Hz) [5]; **4**: δ 248.2 (J_{WC} = 186.7 Hz)] [10]).



(2)

The reactions of the triphenylphosphine-substituted alkylidyne complexes *cis*-[W(CPh)Cl(CO)$_2$(PPh$_3$)$_2$] (***cis-5***) [4] and *trans*-[W(CPh)Cl(CO)$_2$(PPh$_3$)$_2$] (***trans-5***) [5] with dithiocarbamate ligands take a different course than the reactions of the trimethylphosphine analogs. Substitution of triphenylphosphine to give [W(CPh)(S$_2$-CNMe$_2$)(CO)$_2$(PPh$_3$)] (**6**) rather than alkylidyne–carbonyl coupling, is observed in the reaction of ***cis-5*** with dimethyldithiocarbamate (eqn. 3). The presence of only one triphenylphosphine ligand in product **6** is evident from the ^{13}C NMR signals of the carbonyl and alkylidyne carbon atoms, which all appear as doublets due to coupling with only a single phosphorus atom. Reaction of **trans-5** with diethyldithiocarbamate leads to a complex mixture of products which could not be separated. The IR spectrum of the reaction mixture indicates that loss of carbon monoxide is occurring and that no ketenyl species are formed.



(3)

The coordinative lability of one trimethylphosphine ligand in complex **3** had previously been demonstrated. For example, reaction of complex **3** in hot pyridine gives *trans*-[W(CPh)Cl(CO)(py)(PMe$_3$)$_2$] [5,11]. Thus despite the established ability of dithiocarbamate to induce alkylidyne–carbonyl coupling, substitution of PMe$_3$ is observed in the reaction shown in eqn. 2. A possible electronic reason for the lack of alkylidyne–carbonyl coupling in this reaction could consist in the fact that alkylidyne–carbonyl coupling in the monocarbonyl complex **3** would result in a carbonyl-free ketenyl complex. The absence of a good π acceptor ligand to stabilize filled metal d orbitals in the coupling product may negatively affect the coupling process. The difference in reactivity of complexes **1** and **5** towards dithiocarbamate is presumably a consequence of the different steric and electronic properties of trimethylphosphine and triphenylphosphine ligands. Triphenylphosphine is a weaker donor than trimethylphosphine and sterically more demanding. The lower electron density of the metal center in complexes **5** compared to complexes **1**, is expected to reduce the propensity for alkylidyne–carbonyl coupling and thus favor substitution of triphenylphosphine as an alternative reaction pathway [12]. The stronger steric interactions between the triphenylphosphine ligands in *cis*-**5** also facilitate substitution of triphenylphosphine.

TABLE 1. Crystallographic data for **4**

Crystal parameters	
Molecular formula	$C_{19}H_{33}NOP_2S_2W$
Formula weight (g)	601.5
Crystal color	Red
Crystal size (mm^3)	0.12×0.20×0.30
a (Å)	9.387(2)
b (Å)	11.801(3)
c (Å)	11.961(3)
β (deg)	103.71(2)
V (Å^3)	1287.2(5)
Z	2
Space group	$P2_1$
ρ (calc), g cm^{-3}	1.55
$F(000)$	595 e$^-$
μ(Mo$K\alpha$), cm^{-1}	50.3
Transmission coefficients	
Maximum	0.166
Minimum	0.102
Data measurements	
Diffractometer	Nicolet R3m
Radiation	Mo $K\alpha$
Monochromator	Graphite single crystal
2θ range (deg)	3–50
Scan type	ω
Scan speed (deg–min^{-1})	3.91–29.30
Scan width (deg)	1.00
Reflections measured	$\pm h+k+1$
Unique reflections	2389
Observed reflections	1989
Parameters	186
R	0.051
R_w	0.051
GOF	1.12

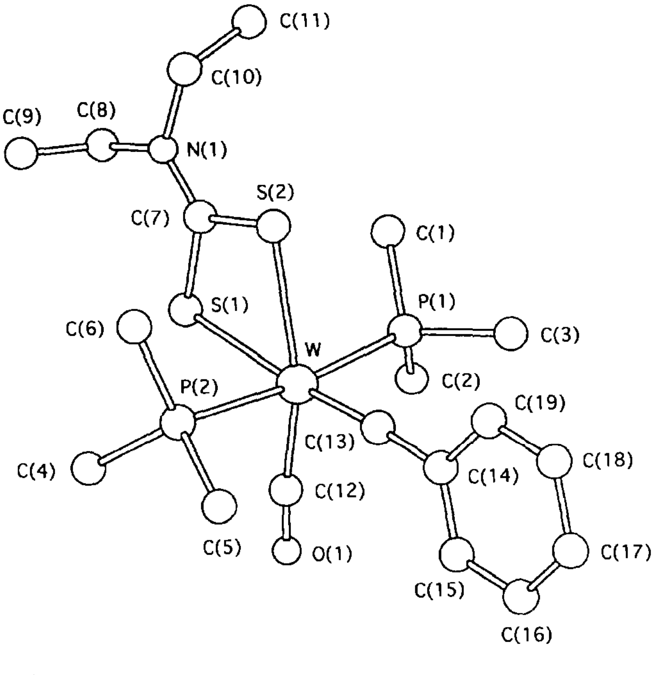


Fig. 1. Molecular structure of compound **4**.

The solid state structure of complex **4** was determined by X-ray crystallography and is shown in Fig. 1. Crystallographic data for **4** are presented in Table 1. The final atomic positional parameters are listed in Table 2. Selected bond distances and bond angles are shown in Table 3. The bond distance between the central tungsten atom and the benzylidyne carbon atom [W–C(13) 1.82(2) Å] is normal [3]. The metal–carbonyl distance [W–C(12) 1.94(3) Å] is somewhat shorter than found in most tungsten alkylidyne complexes. The bonding angle between the alkylidyne ligand and the carbonyl ligand [C(12)–W–C(13)] is 90(2)°. Considering that the dithiocarbamate ligand has only a small bite angle [S(1)–W–S(2) 67.2(2)°] and is located in the same plane as the alkylidyne and carbonyl ligands (Fig. 2), this angle of 90° is remarkably small. The other two coordination angles in this plane are significantly larger [S(1)–W–C(12) 94.9(7)° and S(2)–W–C(13) 108(2)°]. The angles between multiply bonded ligands and adjacent ligands are normally larger than 90°. In the absence of obvious steric reasons this may indicate a slight electronic attraction between the alkylidyne and carbonyl ligands [13]. The dithiocarbamate ligand is bonded almost symmetrically to the metal center. The distance between tungsten and the sulfur atom *trans* to the alkylidyne ligand [W–S(1) 2.647(6) Å] is only slightly longer than the distance between tungsten and the sulfur atom trans to the carbonyl ligand [W–S(2) 2.623(6) Å].

Owing to the coplanar arrangement of alkylidyne, carbonyl, and dithiocarbamate ligands (Fig. 2), the lone pair of one sulfur atom [S(2)] is facing directly the filled metal d orbital which is engaged in π backbonding to the carbonyl ligand. This situation may cause an

TABLE 2. Atomic coordinates (×10^4) and isotropic thermal parameters (Å^2 ×10^3)

	x	*y*	*z*	*U*
W	2262(1)	0	2119(1)	57(1) [a]
P(1)	−250(4)	−4(12)	810(4)	71(2) [a]
C(1)	−1528(30)	949(41)	1148(44)	229(27) [a]
C(2)	−1434(39)	−1258(27)	801(31)	128(15) [a]
C(3)	−289(25)	194(34)	−662(16)	110(11) [a]
P(2)	4630(5)	175(10)	3555(4)	89(2) [a]
C(4)	6139(42)	−311(35)	2844(39)	131(13)
C(5)	4592(58)	−789(32)	4827(31)	131(13)
C(6)	5005(53)	1694(23)	4084(39)	131(13)
C(4′)	5561(62)	1491(33)	3136(46)	132(12)
C(5′)	5780(63)	−1129(34)	3428(45)	132(12)
C(6′)	4449(50)	322(45)	5103(24)	132(12)
S(1)	938(6)	304(6)	3819(5)	90(3) [a]
S(2)	1771(6)	2143(5)	2474(4)	69(2) [a]
C(7)	950(15)	1771(15)	3586(15)	58(6) [a]
N(1)	430(17)	2522(15)	4159(15)	79(7) [a]
C(8)	−305(25)	2144(20)	5120(18)	86(10) [a]
C(9)	708(39)	2247(24)	6161(22)	149(17) [a]
C(10)	253(25)	3724(17)	3854(19)	80(8) [a]
C(11)	−1255(30)	3982(22)	3089(220)	111(12) [a]
C(12)	2386(18)	−1632(26)	2283(18)	95(10) [a]
O(1)	2313(25)	−2618(19)	2284(22)	156(14) [a]
C(13)	3138(15)	−71(31)	920(13)	64(6) [a]
C(15)	4344(16)	−1270(9)	−245(11)	82(6)
C(16)	5027	−1415	−1152	108(8)
C(17)	5253	−484	−1808	107(8)
C(18)	4795	591	−1558	113(8)
C(19)	4111	736	−652	83(6)
C(14)	3885	−194	4	55(4)

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor

TABLE 3

Bond lengths (Å)			
W–P(1)	2.502(4)	W–P(2)	2.475(5)
W–S(1)	2.647(6)	W–S(2)	2.623(6)
W–C(12)	1.94(3)	W–C(13)	1.82(2)
P(1)–C(1)	1.76(4)	P(1)–C(2)	1.85(4)
P(1)–C(3)	1.77(2)	P(2)–C(4)	1.91(5)
P(2)–C(5)	1.91(4)	P(2)–C(6)	1.91(3)
P(2)–C(4′)	1.91(5)	P(2)–C(5′)	1.91(5)
P(2)–C(6′)	1.91(3)	S(1)–C(7)	1.75(2)
S(2)–C(7)	1.74(2)	C(7)–N(1)	1.29(3)
N(1)–C(8)	1.54(3)	N(1)–C(10)	1.47(3)
C(8)–C(9)	1.38(3)	C(10)–C(11)	1.52(3)
C(12)–O(1)	1.17(4)	C(13)–C(14)	1.44(2)
Bond angles (deg)			
P(1)–W–P(2)	173.0(3)	P(1)–W–S(1)	86.4(2)
P(2)–W–S(1)	87.9(2)	P(1)–W–S(2)	85.8(3)
P(2)–W–S(2)	88.3(3)	S(1)–W–S(2)	67.2(2)
P(1)–W–C(12)	95.0(6)	P(2)–W–C(12)	89.4(6)
S(1)–W–C(12)	94.9(7)	S(2)–W–C(12)	162.0(7)
P(1)–W–C(13)	92.4(4)	P(2)–W–C(13)	93.0(4)
S(1)–W–C(13)	175.(2)	S(2)–W–C(13)	108.(2)
C(12)–W–C(13)	90.(2)	W–P(1)–C(1)	117.(2)
W–P(1)–C(2)	119.(2)	C(1)–P(1)–C(2)	94.(2)
W–P(1)–C(3)	114.6(8)	C(1)–CP(1)–C(3)	107.(2)
C(2)–CP(1)–C(3)	103.(2)	W–P(2)–C(4)	108.(2)
W–P(2)–C(5)	109.(2)	C(4)–P(2)–C(5)	109.(2)
W–P(2)–C(6)	112.(2)	C(4)–P(2)–C(6)	110.(2)
C(5)–P(2)–C(6)	109.(2)	W–P(2)–C(4′)	106.(2)
W–P(2)–C(5′)	108.(2)	C(4′)–P(2)–C(5′)	109.(2)
W–P(2)–C(6′)	114.(2)	C(4′)–P(2)–C(6′)	109.(2)
C(5′)–P(2)–C(6′)	109.(2)	W–S(1)–C(7)	89.4(7)
W–S(2)–C(7)	90.4(6)	S(1)–C(7)–S(2)	113.(2)
S(1)–C(7)–N(1)	125.(2)	S(2)–C(7)–N(1)	122.(2)
C(7)–N(1)–C(8)	120.(2)	C(7)–N(1)–C(10)	125.(2)
C(8)–N(1)–C(10)	115.(2)	N(1)–C(8)–C(9)	108.(2)
N(1)–C(10)–C(11)	112.(2)	W–C(12)–O(1)	172.(2)
W–C(13)–C(14)	176.(2)		

increase in energy of this occupied metal d orbital. As a consequence, π backbonding to the carbonyl ligand strengthens. This conclusion is supported by the low IR stretching frequency of the carbonyl ligand in **4**. The smaller *trans* angle between the carbonyl ligand and dithiocarbamate [S(2)–W–C(12) 162.0(7)°], compared to the *trans* angle between the alkylidyne ligand and dithiocarbamate [S(1)–W–C(13) 175 (2)°], could be a consequence of the repulsive interaction between the high-lying occupied metal d orbital and the dithiocarbamate π orbital on S(2).

The alkylidyne complex **4** easily takes up carbon monoxide to generate the ketenyl complex **2** (eqn. 4). This reaction occurs in solution as well as in the solid state. When carbon monoxide is bubbled into a solution of **4**, *e.g.* in THF, at room temperature, the brown-orange solution turns purple immediately. When powdered **4** is placed in a flask under an atmosphere of carbon monoxide, the solid turns slowly purple. After 2 days, the solid consists of about 60% complex **2**. A brown dried blot of **4** on filter paper turns purple within 2 h when placed under an atmosphere of carbon monoxide. The formation of **2** from **4** is reversible (eqn. 4). Upon heating of a solution of **2** in toluene to 100°C, complex **4** forms quantitatively within less than 10 min. Heating of a powdered solid sample of **2** to 100°C

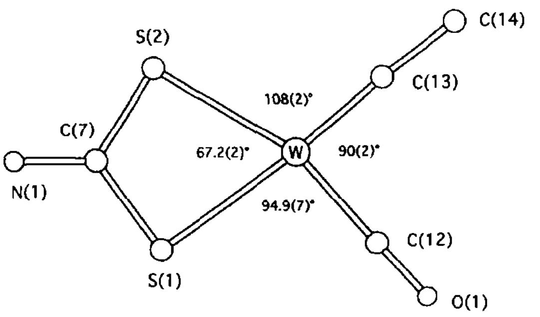
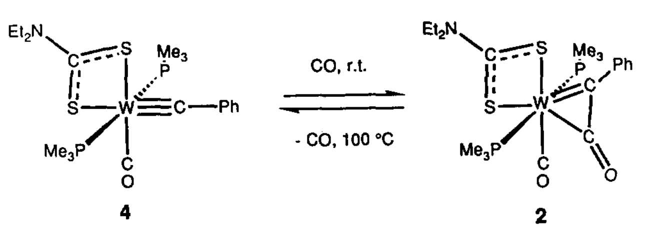


Fig. 2. Partial molecular structure of complex 4. View of the plane containing alkylidyne, carbonyl and dithiocarbamate ligands.

under vacuum, leads to decomposition. Under the proper conditions, complex **4** is thus a reversible carrier of carbon monoxide.



(4)

3. Experimental section

Standard inert-atmosphere techniques were used in the execution of the experiments. The solvents methylene chloride (CaH$_2$), tetrahydrofuran (Na/benzophenone), pentane, and hexane (CaH$_2$) were dried and distilled prior to use. Reagents were obtained from commercial sources and used without further purification. NaS$_2$CNEt$_2$ was dried at 110°C under vacuum for 6 h prior to use. The NMR spectra were measured at magnetic field strengths of 5.87 or 7.05 T (250 or 300 MHz for ^{1}H NMR) in CDCl$_3$ at room temperature unless otherwise noted; solvent peaks were used as internal reference, the data are reported in δ relative to TMS. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory.

3.1. [W(OCCPh)(S$_2$CNEt$_2$)(CO)(PMe$_3$)$_2$] (2) from cis-1

Complex *cis*-**1** (0.77 g, 1.5 mmol) is dissolved in 30 ml THF. Sodium diethyldithiocarbamate (0.31 g, 1.8 mmol) is added, and the solution is stirred at room temperature for 16 h. The solvent is removed under vacuum and the residue recrystallized from pentane (~ 250 ml) to give a deep purple microcrystalline solid (0.85 g, 90%): mp, 124°C dec; IR (CH$_2$Cl$_2$, cm^{-1}) 1871 (s, CO), 1686 (m, CCO), 1493 (m, NCS$_2$);(KBr, cm^{-1}) 1889 (s, CO), 1685 (m, CCO); ^{1}H NMR (CDCl$_3$, 298 K) δ 7.74 (d, 2H, $^3J = 6.9$ Hz) (*o*-Ph), 7.40 (t, 2H, $^3J =$ 7.1 Hz, *m*-Ph), 7.28 (t, 1H, $^3J = 7.3$ Hz, *p*-Ph), 3.80 (q, 2H, $^3j = 7.2$ Hz, NCH_2CH$_3$), 3.66 (q, 2H, $^3J = 7.2$ Hz, NCH_2CH$_3$), 1.34–1.16 (6H, NCH$_2$CH_3), 1.29 (virtual t, 18H, 3.9 Hz, P(CH$_3$)$_3$); ^{13}C {^{1}H} NMR (CDCl$_3$, 253 K) δ 224.0 (t, $J_{WC} = 150.8$ Hz, $^2J_{PC} = 6.6$ Hz, CO), 206.7, 205.1 (S$_2$C and PhCCO), 202.9 (t, $J_{WC} = 53.9$ Hz, $^2J_{PC} = 8.2$ Hz, Ph*C*CO), 141.3 (*i*-Ph), 128.8, 126.7, 126.5 (Ph), 44.2 (N*C*H$_2$CH$_3$), 43.9 (N*C*H$_2$CH$_3$), 15.7 (virtual t, 14.4 Hz, P(CH$_3$)$_3$), 12.6 (NCH$_2$*C*H$_3$), 12.3 (NCH$_2$ *C*H$_3$). Anal. Calcd. for C$_{20}$H$_{33}$NO$_2$P$_2$S$_2$W (MW 629.40): C, 38.17; H, 5.28. Found: C, 38.37; H, 5.43%.

3.2. [W(OCCPh)(S$_2$CNEt$_2$)(CO)(PMe$_3$)$_2$] (2) from ***trans-1***

Isomerization of ***cis*-1** to ***trans*-1** is achieved in CH$_2$Cl$_2$ solution by irradiation with visible light (300 W projector lamp, distance 20 cm) for 3 h. ***Trans-1*** is purified by chromatography on silica gel at −30°C, using a 2:1 mixture of hexane/CH$_2$Cl$_2$ as the eluent. The solvent is removed *in vacuo*. Complex ***trans*-1** (0.294 g, 0.57 mmol) is redissolved in 30 ml THF. Then sodium diethyldithiocarbamate (0.128 g, 0.57 mmol) is added, and the solution is stirred at room temperature for 1.5 h. The solvent is removed under vacuum, and the residue recrystallized from CH$_2$Cl$_2$/hexane (0.335 g, 88.5%). The product is identical with that obtained from *cis*-**1** without prior irradiation.

3.3. [W(CPh)(S$_2$CNEt$_2$)(CO)(PMe$_3$)$_2$] (4)

Complex **3** (1.13 g, 2.0 mmol) is dissolved in 40 ml THF. Sodium diethyldithiocarbamate (0.43 g, 2.5 mmol) is added, and the solution is stirred in a 45°C water bath for two hours until no starting material can be detected by IR. The solvent is removed under vacuum, and the product is recrystallized from pentane (~ 150 ml) to give large brown crystals (1.13 g, 94%): mp, 129°C dec; IR (CH$_2$Cl$_2$, cm^{-1}) 1848 (s, CO), 1485 (m, NCS$_2$); (KBr, cm^{-1}) 1848 (s, CO); ^{1}H NMR (CDCl$_3$, 298 K) δ 7.13 (m, 5H, Ph), 3.77 (q, 2H, $^3J = 7.1$ Hz, NCH_2CH$_3$), 3.67 (q, 2H, $^3J = 7.1$ Hz, NCH_2CH$_3$), 160 (virtual t, 18H, 3.3 Hz, P(CH$_3$)$_3$), 1.30 (t, 3H, $^3J = 7.0$ Hz, NCH$_2$CH_3), 1.21 (t, 3H, $^3J =$ 7.0 Hz, NCH$_2$CH_3); ^{13}C NMR (CDCl$_3$, 243 K) δ 271.2 (t, $J_{WC} = 197.5$ Hz, $^2J_{PC} = 11.7$ Hz, CPh), 248.2 ($J_{WC} =$ 186.7 Hz, CO), 207.1 (S$_2$CN), 152.2 (*i*-Ph), 127.2 (d, $J_{CH} = 172.2$ Hz, *o,m*-Ph), 124.2 (d, $J_{CH} = 164.8$ Hz, *p*-Ph), 44.4 (t, $J_{CH} = 142.6$ Hz, N*C*H$_2$CH$_3$), 44.0 (t, J_{CH} $= 141.9$ Hz, N*C*H$_2$CH$_3$), 18.6 (q, $J_{CH} = 130.3$ Hz, P(CH$_3$)$_3$), 12.4 (q, $J_{CH} = 128.1$ Hz, NCH$_2$*C*H$_3$). Anal. Calcd. for C$_{19}$H$_{33}$NOP$_2$S$_2$W (MW 601.39): C, 37.94; H, 5.31. Found: C, 37.52; H, 5.33%.

3.4. [W(CPh)(S$_2$CNMe$_2$)(CO)$_2$(PPh$_3$)] (6)

Complex **5** (0.889 g, 1.00 mmol) is dissolved in THF (50 ml) and with stirring NaS$_2$CNMe$_2$ (0.143 g, 1.00 mmol) is added. Immediately, the golden solution turns red-brown. After 30 min, the solvent is removed *in vacuo*. The brownish solid is dissolved in a minumum amount of CH$_2$Cl$_2$ (10 ml) and chromatographed on silica (2 × 15 cm) at −30°C, eluting initially with pure pentane to remove any free PPh$_3$. The product is then eluted with a mixture of CH$_2$Cl$_2$/pentane 1:1 (400 ml). Removal of the solvent and recrystallization from CH$_2$Cl$_2$/pentane gives red-orange crystals (0.37 g, 52%) (mp. 110–113°C). IR (CH$_2$Cl$_2$, cm^{-1}) 1980 (s, CO), 1900 (s, CO). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.79–7.16 (m, 20H, C_6H_5), 2.88 (s, hr, 3H, NCH_3), 2.77 (s, br, 3H, NCH_3). ^{13}C $\{^1H\}$ NMR ($CDCl_3$): δ 280.4 (CPh, $J_{PC} = 12$ Hz), 220 (d, $J_{PC} = 9$ Hz, CO), 206.9 (S_2CNMe_2), 204.0 (d, $J_{PC} = 74$ Hz, CO), 150.6 (i-Ph$_{\text{alkylidyne}}$), 137.2 (d, i-Ph), 134–126 (C_6H_5), 39.3 (NCH_3). Anal. Cald. for $C_{30}H_{26}NO_2PS_2W$ (MW = 739.54): C, 50.65; H, 3.68. Found: C, 50.29; H, 3.68%.

3.5. *Reaction of complex 4 with carbon monoxide*

At room temperature, carbon monoxide is bubbled through a solution of **4** in an organic solvent (THF, CH_2Cl_2, and hexane). The solution turns purple immediately. Formation of complex **2** is confirmed by IR and ^1H NMR.

A powdered sample of **4** is placed in a flask under an atmosphere of carbon monoxide. The surface of the sample turns gradually darker. After 2 days, a sample of the powder is dissolved in CH_2Cl_2, and the IR spectrum is taken. The solid consists of about 60% **2** and 40% **4**.

A drop of a solution of **4** in CH_2Cl_2 is blotted onto filter paper. The filter paper is dried and placed in a flask under an atmosphere of carbon monoxide. The brown blot turns purple within about 2 h.

3.6. *Pyrolysis of complex 2*

Upon heating of a solution of **2** in toluene to 100°C, the purple color of the solution turns orange brown within less than 10 min. ^1H NMR indicates clean and complete conversion of **2** to **4**.

A powdered sample of **2** is heated under vacuum to 100°C. The color of the sample turns black. Complex **4** is not formed in significant amounts.

3.7. *Structure determination of 4*

A single crystal of $C_{19}H_{33}NOP_2S_2W$ measuring $0.12 \times 0.20 \times 0.30$ mm was mounted on a glass fiber and centered on a Nicolet R3m diffractometer. Cell constants and their esd's were determined by a least-squares fit of 23 diffractometer-measured reflections with $20° < 2\theta < 25°$. The material belongs to the monoclinic crystal class, space group $P2_1$, with $a = 9.387(2)$ Å, $b = 11.801(3)$ Å, $c = 11.961(3)$ Å, and $\beta = 103.71(2)°$. A density of 1.55 g cm^{-3} was calculated for $Z = 2$, FW = 601.5 g, and a unit cell volume of 1287.2(5) $Å^3$.

All intensity measurements were made at room temperature using graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å) and an ω-scan technique with a variable scan rate of 3.91–29.30°/min. Background counts were taken for half the scan time at each extreme of the scan range. All data (2508) having $k,l \geq 0$ with $3° \leq 2\theta \leq 50°$ were measured in this manner. Crystal decomposition was monitored throughout data collection by remeasuring two standard reflections after every 50 data measurements; a 10% linear decline in intensity was observed. The intensities were reduced by applying Lorentz, polarization, and decay corrections. Empirical absorption corrections were applied based on the azimuthal scans of 10 reflections with $\chi = \pm 90 \pm 20°$. Systematically absent reflections were eliminated and equivalent reflections were averaged to give 2389 unique data of which 1989 were considered to be observed $[\,|F_o| > 3\sigma|F_o|\,]$.

The structure was solved by standard heavy atom techniques. Following several cycles of least-squares refinement, difference Fourier maps displayed large residual peaks around one trimethylphosphine group. A second position was entered for each methyl group and the two positions were each assigned occupancies of 1/2. Hydrogen atoms on the disordered methyl groups were not included; all other hydrogen atoms were included in refinement at idealized positions (C–H 0.96 Å, C–C–H 109° or 120°, $B(H) = 1.2 \times B(C)$). In the final cycles of blocked-cascade least-squares refinement, the phenyl group was refined as a rigid body with fixed (1.395 Å) C–C distance and variable isotropic temperature factors, the disordered methyl groups were fixed as idealized tetrahedra with a variable P–C distance, and all other nonhydrogen atoms were refined with anisotropic temperature factors. Refinement converged at $R = 0.051$, $R_W = 0.051$. Several large peaks in a final difference map (max $e^-/Å^3 = 1.38$) were in the vicinity of the tungsten atom and near the disordered trimethylphosphine group. The quantity minimized by the least-squares program was $\Sigma_w(|F_o| - |F_c|)^2$ where w is the weight of a given observation ($w^{-1} = \sigma^2(|F_o|) + g|F_o|^2$; final value of $g = 0.00135$). The analytical forms for the scattering factors of the neutral atoms were used [14].

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