

IMPROVED PREPARATION OF TERTIARY PHOSPHINE AND RELATED SUBSTITUTION PRODUCTS OF GROUP VI METAL CARBONYLS

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SUMMARY

The substitution of carbon monoxide in the Group VI metal carbonyls by tertiary phosphines, arsines, stibines or certain tertiary amines in boiling ethanol is strongly catalysed by sodium borohydride. This catalysis has been used to prepare a wide range of known and new substituted carbonyls of chromium, molybdenum and tungsten.

INTRODUCTION

Despite considerable investigation, very few well-characterised complexes of the type $\text{MX}_n(\text{QR}_3)_m$ ($\text{M} = \text{Mo}$ or W ; $\text{X} = \text{halogen}$; $\text{QR}_3 = \text{tertiary phosphines or arsines}$) are known¹. Two approaches to their preparations have been made. The first is by the reaction of tertiary phosphines or arsines with the common metal halides in high oxidation states, *e.g.* MoCl_5 or WCl_6 , or with well-characterised halo-complexes with easily displaceable ligands, *e.g.* $\text{MoCl}_3(\text{MeCN})_3$, or $\text{MoCl}_4(\text{THF})_2$ ^{1b,1c}. The second is by the reaction of the tertiary phosphines or arsines with the metal hexacarbonyls or their simple derivatives, followed by halogenation^{1a,1d}. We have investigated both approaches in this laboratory and prefer the first. The details of the preparations of some molybdenum compounds have appeared² and those concerning tungsten are about to be published³. However, our preliminary investigation of the second approach to the problem led to the discovery of a convenient method of substituting carbon monoxide by tertiary phosphines, tertiary arsines, tertiary stibines or nitrogen donor ligands in the hexacarbonyls of the Group VI metals. By older methods the direct substitution reactions often lead to a mixture of products and, because of the volatility of the carbonyls, require the use of sealed systems. Sometimes to get the required degree of substitution it is necessary to vent the carbon monoxide and then continue the reaction. Alternatively, the phosphine derivative may be prepared by first displacing some carbon monoxide from the hexacarbonyl by ligands such as pyridine⁴ or cyclooctadiene⁵ (which displace two molecules of carbon monoxide) or cycloheptatriene⁶ (which displaces three molecules). These ligands may then be displaced in turn by tertiary phosphines, giving specific products such as *cis*- $\text{M}(\text{CO})_4(\text{PR}_3)_2$ and *fac*- $\text{M}(\text{CO})_3(\text{PR}_3)_3$. This latter synthetic route has the disadvantage that it involves at least two steps from the carbonyls.

We find that sodium borohydride catalyses the substitution reaction and also reduces the tendency of the hexacarbonyls of Group VI elements to volatilise from boiling ethanol solution. Some labile non-volatile intermediate is apparently formed. This property can be exploited for the direct substitution of the hexacarbonyls by nitrogen-, phosphorus-, arsenic-, or antimony-donor ligands. A list of the compounds obtained in this way was as shown in Table 1. In general the standard reaction time of 5 h at reflux temperature was used although highly reactive ligands undergo reaction in a much shorter period (*e.g.* Ph_3P in 0.5 h). The product was induced to crystallise by continued stirring of the cold reaction mixture for up to 12 h. This stirring in the cold appears to be necessary. The structures of the new substituted carbonyl complexes were assigned on the basis of their IR spectra.

TABLE 1

THE REACTIONS OF GROUP VI HEXACARBONYLS WITH LIGANDS IN THE PRESENCE OF SODIUM BOROHYDRIDE

Hexa-carbonyl	Ligand	Product	Yield (%)	$\nu(\text{C}\equiv\text{O})^a$ (cm^{-1})	Ref.
$\text{W}(\text{CO})_6$	PPh_3	<i>trans</i> - $\text{W}(\text{CO})_4(\text{PPh}_3)_2$	70	1892 s	9
$\text{W}(\text{CO})_6$	P-n-BuPh_2	<i>trans</i> - $\text{W}(\text{CO})_4(\text{P-n-BuPh}_2)_2$	50	1883 s	
$\text{W}(\text{CO})_6$	P-n-PrPh_2	<i>trans</i> - $\text{W}(\text{CO})_4(\text{P-n-PrPh}_2)_2$	30	1884 s	
$\text{W}(\text{CO})_6$	PEtPh_2	<i>trans</i> - $\text{W}(\text{CO})_4(\text{PEtPh}_2)_2$	30	1888 s	
$\text{W}(\text{CO})_6$	PMePh_2	<i>fac</i> - $\text{W}(\text{CO})_3(\text{PMePh}_2)_3$	65	1939 s	
				1844 s	10
$\text{W}(\text{CO})_6$	$\text{P}(\text{i-Bu})_2\text{Ph}$	<i>trans</i> - $\text{W}(\text{CO})_4[\text{P}(\text{i-Bu})_2\text{Ph}]_2$	40	1878 s	
$\text{W}(\text{CO})_6$	$\text{P-n-Bu}_2\text{Ph}$	<i>fac</i> - $\text{W}(\text{CO})_3(\text{P-n-Bu}_2\text{Ph})_3$	70	1923 s	
				1818 s	
$\text{W}(\text{CO})_6$	$\text{P-n-Pr}_2\text{Ph}$	<i>trans</i> - $\text{W}(\text{CO})_4(\text{P-n-Pr}_2\text{Ph})_2$	45	1878 s	
$\text{W}(\text{CO})_6$	PEt_2Ph	<i>fac</i> - $\text{W}(\text{CO})_3(\text{PEt}_2\text{Ph})_3$	60	1928 s	
				1828 s	11
$\text{W}(\text{CO})_6$	PMe_2Ph	<i>fac</i> - $\text{W}(\text{CO})_3(\text{PMe}_2\text{Ph})_3$	65	1932 s	
				1833 s	14
$\text{W}(\text{CO})_6$	P-n-Pr_3	<i>trans</i> - $\text{W}(\text{CO})_4(\text{P-n-Pr}_3)_2$	35	1869 s	
$\text{W}(\text{CO})_6$	PEt_3	<i>fac</i> - $\text{W}(\text{CO})_3(\text{PEt}_3)_3$	25	1922 s	
				1818 s	
$\text{W}(\text{CO})_6$	$\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$	$\text{W}(\text{CO})_4(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$	50	2020 m	
				1920 (sh)	
				1903 s	
				1885 (sh)	7
$\text{W}(\text{CO})_6$	$\text{Ph}_2\text{PCH}_2\text{PPh}_2$	$\text{W}(\text{CO})_4(\text{Ph}_2\text{PCH}_2\text{PPh}_2)$	80	2020 m	
				1925 (sh)	
				1909 s	
				1880 (sh)	7
$\text{W}(\text{CO})_6$	$\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$	$\text{W}(\text{CO})_4(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)$	40	2016 m	
				1923 (sh)	
				1893 s	
				1878 (sh)	
$\text{W}(\text{CO})_6$	$\text{CH}_3\text{C}(\text{CH}_2\text{PPh}_2)_3$	$\text{W}(\text{CO})_4[\text{CH}_3\text{C}(\text{CH}_2\text{PPh}_2)_3]$	80	2016 m	
				1924 (sh)	
				1895 s	
				1884 (sh)	

TABLE 1 (continued)

Hexa-carbonyl	Ligand	Product	Yield (%)	$\nu(\text{C}\equiv\text{O})^a$ (cm^{-1})	Ref.
W(CO) ₆	AsPh ₃	<i>cis</i> -W(CO) ₄ (AsPh ₃) ₂	25	2020 m 1917 (sh) 1900 s 1875 (sh)	
W(CO) ₆	AsEt ₃	<i>cis</i> -W(CO) ₄ (AsEt ₃) ₂	25	2012 m 1908 (sh) 1892 s 1862 (sh)	
W(CO) ₆	SbPh ₃	<i>cis</i> -W(CO) ₄ (SbPh ₃) ₂	25	2020 m 1922 (sh) 1907 s 1880 (sh)	
W(CO) ₆	2,2'-Bipyridine	W(CO) ₄ (2,2'-Bipyridine)	80	2009 m 1895 (sh) 1880 s 1840 (sh)	12
W(CO) ₆	<i>o</i> -Phenanthroline	W(CO) ₄ (<i>o</i> -Phenanthroline)	50	2010 m 1902 (sh) 1879 s 1838 (sh)	13
Mo(CO) ₆	PPh ₃	<i>trans</i> -Mo(CO) ₄ (PPh ₃) ₂	90	1901 s	9
Mo(CO) ₆	Ph ₂ PCH ₂ CH ₂ PPh ₂	Mo(CO) ₄ (Ph ₂ PCH ₂ CH ₂ PPh ₂)	80	2021 m 1926 (sh) 1909 s 1884 (sh)	7
Mo(CO) ₆	CH ₃ C(CH ₂ PPh ₂) ₃	Mo(CO) ₄ [CH ₃ C(CH ₂ PPh ₂) ₃]	85	2019 m 1928 (sh) 1906 s 1889 (sh)	
Mo(CO) ₆	AsPh ₃	<i>cis</i> -Mo(CO) ₄ (AsPh ₃) ₂	60	2025 m 1927 (sh) 1914 s 1886 (sh)	15
Mo(CO) ₆	SbPh ₃	<i>cis</i> -Mo(CO) ₄ (SbPh ₃) ₂	70	2023 m 1931 (sh) 1921 s 1897 (sh)	16
Cr(CO) ₆	PPh ₃	<i>trans</i> -Cr(CO) ₄ (PPh ₃) ₂	45	1890 s	9
Cr(CO) ₆	AsPh ₃	Cr(CO) ₅ (AsPh ₃)	10	2066 m 1988 (sh) 1940 s	17
Cr(CO) ₆	SbPh ₃	<i>cis</i> -Cr(CO) ₄ (SbPh ₃) ₂	10	2008 m 1984 (sh) 1922 (sh) 1904 s 1883 (sh)	18
Cr(CO) ₆	CH ₃ C(CH ₂ PPh ₂) ₃	Cr(CO) ₄ [CH ₃ C(CH ₂ PPh ₂) ₃]	60	2000 m 1915 (sh) 1875 s 1825 (sh)	

^a In chloroform.

Substitution apparently occurs stepwise but we had no indication of significant amounts of substitution products other than those which were isolated. Where yields are low, the greater part of the hexacarbonyl is recovered unchanged, indicating that the substitution intermediate is labile. The magnitude of the catalytic effect of the sodium borohydride is indicated by comparing the reaction of tungsten hexacarbonyl with 1,2-bis(diphenylphosphino)ethane which, by our method, gives a 50% yield of pure $W(CO)_4(Ph_2PCH_2CH_2PPh_2)$ in 5 h at 80°, but in the absence of borohydride only minute quantities of product are formed. Also the reaction mixture develops a yellow colour when borohydride is present, but stays colourless in its absence. Direct substitution in the absence of ethanol and borohydride requires the use of a sealed system (17 h, 150°, 60% yield)⁷.

We have not investigated the mechanism of the catalysis. Generally substitution into metal hexacarbonyls involves primary dissociation of carbon monoxide from the carbonyl, which is slow⁸. Since our reaction is relatively fast it seems likely that the initial step is attack by hydride ion either at carbon or, less likely, into the co-ordination shell of the metal to give a relatively labile intermediate salt. Neither pyridine nor sodium ethoxide in alcohol catalyses the substitution.

EXPERIMENTAL

Microanalyses were carried out by Mr. A. G. Olney, The Chemical Laboratory, The University of Sussex, melting points were determined in sealed, evacuated tubes, molecular weights were determined in 1,2-dichloroethane using a Hitachi-Perkin-Elmer molecular-weight bridge, conductivities were measured in nitrobenzene solution using a Portland Electronics conductivity bridge, infrared spectra were determined using a Unicam SP1200 spectrophotometer, and magnetic moments were measured using a Faraday balance.

Reactions, except those involving liquid phosphines, were carried out in air. Industrial methylated spirit was used as reaction medium. The mole ratio of ligand to hexacarbonyl was generally 3/1, although where products of the type $M(CO)_4L_2$ were obtained the isolation was easier when a mole ratio of 2/1 was used. Using an excess of ligand did not force a greater degree of substitution than shown in Table 1, and even $CH_3C(CH_2PPh_2)_3$ displaced only two carbon monoxide molecules from chromium, molybdenum and tungsten carbonyls, as shown by IR and analysis. A typical preparation is described.

fac-Tricarbonyltris(dimethylphenylphosphine)tungsten(0)

Tungsten hexacarbonyl (2.7 g), sodium borohydride (0.8 g) and dimethylphenylphosphine (3.2 g) were heated together in methylated spirit (150 ml) under gentle reflux for 5 h. The reaction mixture was stirred and allowed to crystallise at room temperature overnight. The crystals were filtered off, washed repeatedly with water and then with ethanol, and dried in air (3.2 g, 65%). The product was recrystallised from dichloromethane/methanol. (Found: C, 47.6; H, 5.09; Mol.wt., 634. $C_{27}H_{33}O_3P_3W$ calcd.; C, 47.5; H, 4.87%; Mol.wt., 682.

When P-n-Pr₂Ph and P-i-Bu₂Ph were used, the reaction mixtures were evaporated to half the original volume before filtration. Aqueous ethanol as reaction medium with PEt₃, PPr₃ and AsEt₃ gave a better separation of product.

TABLE 2

NEW DERIVATIVES OF GROUP VI B HEXACARBONYLS

Compound	Colour and crystal form	M.p. (°C)	Analyses found (calcd.) (%)	
			C	H
<i>trans</i> -W(CO) ₄ (P- <i>n</i> -BuPh ₂) ₂	Yellow prisms	180–181	55.4 (55.4)	4.89 (4.87)
<i>trans</i> -W(CO) ₄ (P- <i>n</i> -PrPh ₂) ₂ ^a	Yellow plates	173–174	54.3 (54.3)	4.65 (4.52)
<i>trans</i> -W(CO) ₄ (PEtPh ₂) ₂	Yellow needles	154–155 (decompn.)	52.7 (53.1)	4.26 (4.17)
<i>trans</i> -W(CO) ₄ [P(<i>i</i> -Bu) ₂ Ph] ₂ ^{a,b}	Yellow prisms	115–116	52.5 (51.9)	6.48 (6.22)
<i>fac</i> -W(CO) ₃ (P- <i>n</i> -Bu ₂ Ph) ₃	White prisms	160–161 (decompn.)	58.7 (57.8)	8.10 (7.44)
<i>trans</i> -W(CO) ₄ (P- <i>n</i> -Pr ₂ Ph) ₂ ^c	Yellow prisms	112–114	49.2 (49.1)	5.70 (5.56)
<i>trans</i> -W(CO) ₄ (P- <i>n</i> -Pr ₃) ₂	Yellow prisms	127–128	42.4 (42.7)	6.96 (6.83)
W(CO) ₄ [CH ₃ C(CH ₂ PPh ₂) ₃]	Light yellow prisms	210 (decompn.)	58.4 (58.7)	4.24 (4.24)
<i>cis</i> -W(CO) ₄ (AsPh ₃) ₂	Yellow prisms	204–205 (decompn.)	52.9 (52.8)	3.41 (3.35)
<i>cis</i> -W(CO) ₄ (AsEt ₃) ₂	Light yellow needles	69–70	31.3 (31.0)	4.86 (4.88)
<i>cis</i> -W(CO) ₄ (SbPh ₃) ₂	Light yellow prisms	190–191	48.0 (47.9)	3.03 (3.00)
Mo(CO) ₄ [CH ₃ C(CH ₂ PPh ₂) ₃]	White prisms	215 (decompn.)	64.7 (64.9)	4.96 (4.69)
Cr(CO) ₄ [CH ₃ C(CH ₂ PPh ₂) ₃]	Yellow plates	276	68.6 (68.5)	5.31 (4.94)

^a Non-electrolytes, others not tested. ^b Mol.wt. 736; calcd.: 740. ^c Mol.wt. 696; calcd.: 684.

REFERENCES

- (a). *e.g.* J. LEWIS, R. S. NYHOLM, C. S. PANDE AND M. H. B. STIDDARD, *J. Chem. Soc.*, (1963) 3600.
(b). E. A. ALLEN, K. FEENAN, AND G. W. A. FOWLES, *J. Chem. Soc.*, (1965) 1636.
(c). P. M. BOORMAN, N. N. GREENWOOD AND M. A. HILDON, *J. Chem. Soc. A*, (1968) 2466.
(d). M. MOSS AND B. L. SHAW, *J. Chem. Soc. A*, (1970) 545; and references in these.
- A. V. BUTCHER AND J. CHATT, *J. Chem. Soc. A*, (1970) 2652.
- A. V. BUTCHER, J. CHATT, G. J. LEIGH AND P. L. RICHARDS, to be published.
- e.g.* W. STROHMEIER AND K. GERLACH, *Chem. Ber.*, 93 (1960) 2087.
- E. O. FISCHER AND W. FRÖHLICH, *Chem. Ber.*, 92 (1959) 2995.
- E. W. ABEL, M. A. BENNETT AND G. WILKINSON, *J. Chem. Soc.*, (1959) 2323.
- J. CHATT AND H. R. WATSON, *J. Chem. Soc.*, (1961) 4980.
- G. R. DOBSON, I. W. STOLZ AND R. J. SHELINE, *Advan. Inorg. Chem. Radiochem.*, 8 (1966) 1.
- W. HIEBER AND J. PETERHANS, *Z. Naturforsch.*, 14b (1959) 462.
- B. BELL, J. CHATT AND G. J. LEIGH, *Chem. Commun.*, (1970) 842.
- F. CANZIANI, F. ZINGALES AND N. SARTORELLI, *Gazz. Chim. Ital.*, 94 (1964) 841.
- M. H. B. STIDDARD, *J. Chem. Soc.*, (1962) 4712.
- R. J. ANGELICI AND J. R. GRAHAM, *Inorg. Chem.*, 6 (1967) 988.
- J. M. JENKINS, J. R. MOSS AND B. L. SHAW, *J. Chem. Soc. A*, (1969) 2796.

- 15 G. BOUQUET AND M. BIGORGNE, *Bull. Soc. Chim. Fr.*, (1962) 433.
- 16 D. BENLIAN AND M. BIGORGNE, *Bull. Soc. Chim. Fr.*, (1963) 1583.
- 17 T. A. MAGEE, C. N. MATTHEWS, T. S. WANG AND J. H. WOTIZ, *J. Amer. Chem. Soc.*, 83 (1961) 3200.
- 18 R. DOBSON AND L. W. HOUK, *Inorg. Chim. Acta*, 1 (1967) 287.

J. Organometal. Chem., 29 (1971) 105-110