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Catalysed and Uncatalysed Substitution Reactions of [W(CO)$_5$(NCR)] (R = Me, Et)

CHERYL-ANN DICKSON, ANNE W. McFARLANE and NEIL J. COVILLE*

Department of Chemistry, University of the Witwatersrand, Johannesburg, P O Wits 2050, South Africa

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Abstract

The reaction between [W(CO)$_5$(NCR)] (R = Me, Et) and tBuNC in the presence of PdO yielded both [W(CO)$_4$(CNBut)$_2$] and [W(CO)$_4$(NCR)(CNBut)] and revealed that both RCN and CO are catalytically replaced by tBuNC. Reaction of a 2:1 mixture of [W(CO)$_5$(NCMe)] and PPh$_2$(CH$_2$)$_n$PPh$_2$ (P-P; n = 2, 5) in toluene at 55 °C gave a product mixture consisting of the bridged complex [W(CO)$_5$(P-P)W(CO)$_5$] (dominant product) and the chelate complex [W(CO)$_4$(P-P)]. Unexpectedly when the reaction with PPh$_2$(CH$_2$)$_n$PPh$_2$ (n = 4, 5) was performed in CHCl$_3$ the chelate complex [W(CO)$_4$(P-P)] was the dominant product.

Introduction

The ligand substitution reaction is one of the most well studied of the reaction types in organometallic chemistry. Notwithstanding the simplicity of the stoichiometry of the reaction, many mechanisms have been proposed to explain kinetic and other experimental data obtained for the substitution reaction [1, 2].

$$ML_x \xrightarrow{L'} ML_{x-1}L' + L$$

In some instances the M–L bond strength may be high and consequently alternative strategies to the normal thermal or photochemical [3] approaches must be used to induce ligand replacement. One procedure is to replace the leaving group with an 'intermediate' ligand which can then at a later stage be replaced by the substituting ligand *viz.*

$$ML_x + L'' \longrightarrow ML_{x-1}L'' \xrightarrow{L'} ML_{x-1}L'$$

(L″ = intermediate ligand). This is a particularly useful approach when the conditions required for direct replacement of L by L′ are too harsh and lead to product decomposition.

In recent years the use of NMe$_3$O to induce the CO replacement reaction in metal carbonyl systems has proven to be a general method applicable to a wide range of transition metal carbonyl complexes [4, 5]. Kinetic studies on the displacement of the CO group from a range of metal complexes has established the reaction mechanism – a mechanism in which CO is oxidized to CO$_2$ [6]. The vacant coordination site created by loss of CO as CO$_2$ can readily be filled by a solvent molecule or substituting ligand. This method in particular leads to the ready availability of nitrile substituted derivatives when the reaction is carried out in the presence of a nitrile solvent. The nitrile ligand is regarded as a good leaving group when compared to the starting carbonyl group [7].

In this paper we wish to explore the relative reactivities of a nitrile group and a carbonyl group on the same metal fragment. We chose to investigate the complex [W(CO)$_5$(NCR)] (R = Me, Et) since the complex has a relatively strong W–NCR bond [8] which allows for substitution reactions to be performed at $T > 30$ °C without product decomposition. In particular we wish to report on our results for the following reactions

(i) The relative displacement of RCN and CO from [W(CO)$_5$(NCR)] in the presence of PdO catalysts.

(ii) The reaction of [W(CO)$_5$(NCR)] with chelating diphosphines (PPh$_2$(CH$_2$)$_n$PPh$_2$, n = 1–5).

It is to be noted that the electrochemically induced reaction of [W(CO)$_5$(NCCH$_3$)] with tBuNC [9] and the reaction of [Mo(CO)$_6$] with diphosphines in the presence of NMe$_3$O in CH$_3$CN [10] have both been reported.

Experimental

[W(CO)$_6$] was purchased from Climax Molybdenum Company, CH$_3$CH$_2$CN from Merck Chemicals, CH$_3$CN from SAARCHEM, tBuNC from Fluka A.G. and the diphosphine ligands from Strem Chemicals. NMe$_3$O was purchased from Aldrich Co. Ltd. and dried using a Dean-Stark apparatus (toluene as solvent). Column chromatography was performed on silica gel (Merck 60F, 70–230 mesh). Infrared spectra

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*Author to whom correspondence should be addressed.

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were recorded on a JASCO IRA-1 or a Pye Unicam SP300 and NMR (^1H, ^{31}P) spectra on a Bruker AC 200 NMR spectrometer. Melting point data were recorded on a Kofler micro hot stage apparatus and are uncorrected. Reactions were routinely carried out under nitrogen in degassed and distilled solvents. $[W(CO)_5(CNBut)]$ was prepared by the literature procedure, using PdO as catalyst [11].

*Preparation of [W(CO)₅(NCMe)] [12]**

$[W(CO)_6]$ (0.468 g; 1.33 mmol) was stirred with $(CH_3)_3NO$ (0.115 g; 1.53 mmol) in CH_3CN (10 ml) for approximately 4 h. The solution was pumped to dryness to give the required complex as a yellow solid (76% yield).

Preparation of [W(CO)₅(NCEt)]

$[W(CO)_6]$ (0.929 g; 2.64 mmol) was stirred with $(CH_3)_3NO$ (0.188 g; 2.51 mmol) in CH_3CH_2CN (25 ml) for approximately 1 h. The solution was pumped to dryness to give a mixture of $[W(CO)_5(NCEt)]$ and $[W(CO)_4(NCEt)_2]$. Hexane extraction and column chromatography yielded pure $[W(CO)_5(NCEt)]$ (60% yield), melting point (m.p.) 54.8–55.0 °C.

Preparation of [W(CO)₄(NCEt)(NCBut)] from [W(CO)₅(CNBut)]

$(CH_3)_3NO$ (0.041 g; 0.540 mmol) was added to a solution of $[W(CO)_5(NCBut)]$ (0.200 g; 0.491 mmol) in CH_3CH_2CN (40 ml). The solution was stirred overnight and pumped to dryness to yield $[W(CO)_4(NCEt)(CNBut)]$ (77% yield) characterized by IR and NMR spectroscopy (Table 1).

Catalysed Reaction of [W(CO)₅(NCEt)] and tBuNC

(a) $[W(CO)_5(NCEt)]$ (0.125 g; 0.330 mmol) was reacted with tBuNC (41 μl; 0.363 mmol) in benzene (25 ml). Approximately 10 mg PdO catalyst was added and the reaction monitored by IR spectroscopy. After one hour the reaction appeared complete and the solution was filtered through cellulose and pumped to dryness. The yellow solid obtained was a mixture of $[W(CO)_4(NCEt)(CNBut)]$ and $[W(CO)_4(CNBut)_2]$ as determined by NMR spectroscopy (Table 1).

(b) $[W(CO)_5(NCEt)]$ (0.069 g; 0.188 mmol) was reacted with tBuNC (23 μl; 0.204 mmol) in EtCN (20 ml). Approximately 10 mg PdO catalyst was added and the reaction monitored by IR spectroscopy. After 90 min the solution was filtered through cellulose and pumped to dryness to yield a mixture of $[W(CO)_4(NCEt)(CNBut)]$ and $[W(CO)_4(CNBut)_2]$ (Table 1).

Uncatalysed Reaction of [W(CO)₅(NCEt)] and tBuNC

A solution of tBuNC (41 μl; 0.363 mmol) and $[W(CO)_5(NCEt)]$ (0.125 g; 0.330 mmol) in benzene (25 ml) was stirred overnight. The reaction solution was then pumped to dryness to yield a mixture of starting material and $[W(CO)_5(CNBut)]$.

Catalysed Reaction of [W(CO)₅(NCMe)] and tBuNC

$[W(CO)_5(CNMe)]$ (0.203 g; 0.556 mmol) was reacted with tBuNC (61 μl; 0.548 mmol) in benzene (10 ml). Approximately 10 mg PdO catalyst was added to the stirred solution. After 90 min the reaction mixture was pumped to dryness and yielded a mixture of $[W(CO)_5(CNBut)]$, $[W(CO)_4(CNBut)_2]$ and $[W(CO)_4(NCMe)(CNBut)]$.

Uncatalysed Reaction of [W(CO)₅(NCMe)] and tBuNC

A solution of tBuNC (66 μl; 0.586 mmol) and $[W(CO)_5(NCMe)]$ (0.107 g; 0.293 mmol) in benzene (20 ml) was stirred overnight. The reaction solution was pumped to dryness to yield $[W(CO)_5(CNBut)]$ and a small amount of $[W(CO)_4(CNBut)_2]$.

Reaction Between [W(CO)₅(NCMe)] and PMePh₂

To a $CHCl_3$ solution (20 ml) containing $[W(CO)_5(NCMe)]$ (1 mmol) was added $PMePh_2$ (0.198 g; 1 mmol). The solution was heated at 55 °C for 2 h, filtered and analysed by NMR spectroscopy (Table 2).

TABLE 1. IR and ^1H NMR Data for the Tungsten Complexes

Complex	IR (cm^{-1})^a				NMR δ (ppm)^b		
	ν(CN)	ν(CO)			CH_3	CH_2	tBu
$[W(CO)_5(NCMe)]$			1928s	1909m	2.36		
$[W(CO)_5(NCEt)]$		2030w	1927s	1910s	2.65q	1.39t	
$[W(CO)_5(CNBut)]$	2160w	2070w	1950s	1920s			1.49(0.64^c)
$[W(CO)_4(NCMe)(CNBut)]$	2162w	2020w	1950s	1922m	2.30		1.51(0.86^c)
$[W(CO)_4(NCEt)(CNBut)]$	2128w	2030w	1940s	1915s	2.60q	1.36t	1.51(0.86^c)
$[W(CO)_4(CNBut)_2]$	2140w	2110w	2000m	1905s,br			1.49(0.80^c)

^{a}Recorded in hexane unless otherwise stated. ^{b}Recorded in $CDCl_3$ relative to TMS. ^{c}Recorded in C_6D_6.

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*In non-coordinating solvents, e.g. CH_2Cl_2, $[W(CO)_5(NMe_3)]$ is formed [12].

TABLE 2. Analysis of the Product Distribution for the Reaction [W(CO)$_5$(NCMe)] and PPh$_2$(CH$_2$)$_n$PPh$_2$ (n = 1–5)[a]

PPh$_2$(CH$_2$)$_n$PPh$_2$ n	Reactant ratio[b]	Solvent	Products[c] (%) chelate	bridge
				dangling:
1	1:1	CHCl$_3$	15	0 85
2	1:1	CHCl$_3$	49	51
	2:1	CHCl$_3$	0	100
3	2:1	toluene	22	78
4	2:1	CHCl$_3$	76 (87)[d]	24 (13)[d]
	2:1	toluene	43	57
	5:1	toluene	4	96
5	2:1	CHCl$_3$	73	27
	2:1	toluene	19	81

[a] Analysis by ^{31}P NMR spectroscopy. [b] Ratio [W(CO)$_5$(NCMe)]:PPh$_2$(CH$_2$)$_n$PPh$_2$. [c] Analysis based on the assumption that the only products formed were [W(CO)$_4$PPh$_2$(CH$_2$)$_n$PPh$_2$] (chelate) and [W(CO)$_5$PPh$_2$(CH$_2$)$_n$PPh$_2$W(CO)$_5$] (bridge). The ^{31}P NMR spectra did reveal the presence of minor amounts of other products. [d] Repeat reaction.

Reaction Between [W(CO)$_5$(NCMe)] and Diphosphines PPh$_2$(CH$_2$)$_n$PPh$_2$ (n = 1–5)

(a) [W(CO)$_6$] (0.350 g; 1 mmol) and Me$_3$NO (0.074 g; 1 mmol) were stirred in MeCN (30 ml) at 20 °C until all the reagents had dissolved (30 min). The diphosphine (n = 2; 0.5 mmol) was then added and the reagents were heated at 75 °C for 16 h. At the end of this time no change was observed in the concentration of reactants and product (a product insoluble in CH$_3$CN was formed) as detected by IR spectroscopy and TLC. The solution was pumped to dryness, the crude material washed with hexane and analysed by ^{31}P NMR spectroscopy. Results are shown in Table 2.

(b) [W(CO)$_5$(NCMe)] (1 mmol) and diphosphine (n = 1–5; 0.5 mmol) were refluxed together in CHCl$_3$ (20 ml) at 55 °C in toluene (20 ml) for 2–2½ h. The solution was filtered through cellulose and pumped to dryness. Excess diphosphine was removed by washing with hexane or passage of the crude material through a silica gel column (benzene as eluent). The products were analysed by ^{31}P NMR spectroscopy (Table 2).

Results and Discussion

The reaction of [W(CO)$_6$] with NMe$_3$O in MeCN has been reported [6], and in the absence of other ligands yields [W(CO)$_5$(NCMe)] [12]. This product has been synthesized by alternative routes [8, 13, 14]. The compound is sufficiently stable to be purified by passage through silica gel columns.

In this work we have synthesized [W(CO)$_5$(NCR)] (R = Me, Et) by the NMe$_3$O procedure in good yield (>60%). Small amounts of the disubstituted derivatives are also found but can readily be removed by column chromatography. The ready synthesis of the disubstituted derivative is in keeping with the recently reported kinetic study on the above reaction [7].

The reaction of [W(CO)$_5$(NCR)] with tBuNC at room temperature slowly yielded [W(CO)$_5$(CNBut)]. Even after 24 h large amounts of starting material were still present as detected by TLC. The slow reaction is in keeping with the reported study on the reaction of [W(CO)$_5$(NCMe)] with PPh$_3$ [9]. However addition of PdO to [W(CO)$_5$(NCR)] and tBuNC (CHCl$_3$ or benzene) leads to a dramatic increase in the disappearance of the reactant as detected by IR spectroscopy and TLC. Analysis of the final product mixture by NMR spectroscopy indicates formation of both [W(CO)$_4$(CNBut)$_2$] and [W(CO)$_4$(NCR)(CNBut)] (*ca.* 1:1 ratio in CHCl$_3$; *ca.* 1:2 ratio in C$_6$H$_6$). [W(CO)$_4$(CNBut)$_2$] was identified from the known physical properties of the independently synthesized material [15]. The novel mixed product [W(CO)$_4$(NCEt)(CNBut)] was independently synthesized from [W(CO)$_5$(CNBut)] and EtCN in the presence of NMe$_3$O. The product had identical physical properties to that produced in the PdO reaction above. A possible mechanistic scheme for the synthesis of the products from the PdO reaction is shown below.

$$\begin{tikzcd}
{[\mathrm{W(CO)_5(NCR)}]} \arrow[r, "a"] \arrow[d, "b"] & {[\mathrm{W(CO)_4(NCR)(CNBut)}]} \arrow[d, "d"] \\
{[\mathrm{W(CO)_5(CNBut)}]} \arrow[r, "c"] & {[\mathrm{W(CO)_4(CNBut)_2}]}
\end{tikzcd}$$

At present it is not possible to determine whether [W(CO)$_4$(CNBut)$_2$] is synthesized via route b → c or route a → d. Since the W–CO bond in [W(CO)$_4$(NCR)(CNBut)] is predicted to be stronger than in [W(CO)$_5$(CNBut)], route b → c appears to be the more attractive pathway. Irrespective of the pathway the data are consistent with (i) a catalysed reaction in which CO is displaced prior to RCN even though the thermal reaction gives a result consistent with only M–NCR bond cleavage, and (ii) use of catalysts to displace RCN in the [W(CO)$_{6-x}$(CNR)$_x$] (x = 1) complexes.

The reaction of [W(CO)$_5$(NCR)] in the presence of catalysts suggested to us that the reaction of [W(CO)$_5$(NCR)] with diphosphines (P-P) could give rise to a situation in which the dangling phosphine in the initially formed product [W(CO)$_5$(P-P)] could either react with another [W(CO)$_5$(NCR)] molecule to yield the bridged species [W(CO)$_5$(P-P)W(CO)$_5$]

TABLE 3. IR and ^{31}P NMR Data for the Products Obtained from the Reactions Between $W(CO)_5(NCMe)$ and $PPh_2(CH_2)_nPPh_2$ ($n = 1, 5$)

Complex	IR (cm^{-1})[a]				^{31}P NMR[b]		
					δ (ppm)	J(P–W) (Hz)[c]	J(P–P) (Hz)
$PPh_2CH_2PPh_2$					−21.89[d]		+125[e]
$[W(CO)_5(PPh_2CH_2PPh_2)]$	2070s	1982w	1940vs		+10.45, −24.33	245.7	105.7
$[W(CO)_4(PPh_2CH_2PPh_2)]$	2013s	1909sh	1902vs	1871s [f]	−22.55[g]	201.0[h]	+30.5[i]
$PPh_2(CH_2)_2PPh_2$					−12[j]		+33.6[k]
$[W(CO)_5(PPh_2(CH_2)_2PPh_2)]$	2074s	1986w	1940vs [k]		+13.5	240.0[l]	37.2[l]
$[W(CO)_5]_2PPh_2(CH_2)_2PPh_2$	2070s	1986w	1943vs [m]		+13.17[n]	241.6[o]	36.4[p]
$[W(CO)_4(PPh_2(CH_2)_2FPh_2)]$	2016s	1912sh	1901vs	1876s [q]	+41[r]	228.9[s]	+5.5[i]
$PPh_2(CH_2)_3PPh_2$ [e]					−17.5		1.0
$[W(CO)_5]_2PPh_2(CH_2)_3PPh_2$	2073	1985w	1940vs		9.16	218.5	2.8
$[W(CO)_4(PPh_2(CH_2)_3PPh_2)]$	2018w	1924s	1890m		1.04[t]	222.7[u]	−21.5[i]
$[W(CO)_5]_2PPh_2(CH_2)_4PPh_2$	2070s	1980w	1940vs		9.50	239.0	
$[W(CO)_4(PPh_2(CH_2)_4PPh_2)]$	2017m	1921s	1890vs		11.88[v]	230.7[w]	−15.0[i]
$[W(CO)_5]_2PPh_2(CH_2)_5PPh_2$	2023s	1960w	1920vs		9.80	238.5	
$[W(CO)_4(PPh_2(CH_2)_5PPh_2)]$	1982m	1905s	1870s		9.58	230.7	
$[W(CO)_5(PMePh_2)]$	2072m	1980w	1940vs		−3.08[x]	238.1[y]	
$[W(CO)_4(PMePh_2)_2]$	2015s	1930s	1890s		−3.20	230.8	

[a] Recorded in $CHCl_3$, unless otherwise stated. [b] Recorded in $CDCl_3$, unless otherwise stated. Relative to 85% H_3PO_4. [c] ^{31}P–^{183}W coupling constant. [d] Ref. 17: −23.6; ref. 24: −21.6 (recorded in CH_2Cl_2–C_6D_6 (9:1 v/v). [e] Ref. 24, recorded in CH_2Cl_2–C_6D_6 (9:1 v/v). [f] Ref. 22, recorded in 1,2-dichloroethane; ref. 17 (in cyclohexane): 2022; 1927; 1915; 1896 cm^{-1}. [g] Ref. 17: −23.6; ref. 20 (in THF): −23.0; ref. 21 (in CH_2Cl_2–C_6D_6 (9:1 v/v)): −23.5. [h] Ref. 20 (in THF) and ref. 21 (in CH_2Cl_2–C_6D_6 (9:1 v/v)): −201.2. [i] Ref. 21, recorded in CH_2Cl_2–C_6D_6 (9:1 v/v). [j] Ref. 24: −13.2 (recorded in CH_2Cl_2–C_6D_6 (9:1 v/v)). [k] Ref. 18. [l] Ref. 19, recorded in $CDCl_3$. [m] Ref. 18: 2075; 1983; 1942 cm^{-1}; ref. 16: 2073; 1984; 1943 cm^{-1}. [n] Ref. 16: 12.7. [o] Ref. 16. [p] Ref. 16: 36.6. [q] Ref. 22, recorded in 1,2-dichloroethane; ref. 23: 2012m; 1915sh; 1898s; 1875s. [r] Ref. 20 (in THF): 40.7; ref. 21 (in CH_2Cl_2–C_6D_6 (9:1 v/v)): 40.1; ref. 23 (to P_4O_6): 77.2. [s] Ref. 20, recorded in THF; ref. 21 (in CH_2Cl_2–C_6D_6 (9:1 v/v)): 229; ref. 23: 239.0. [t] Ref. 20 (in THF) and ref. 21 (in CH_2Cl_2–C_6D_6 (9:1 v/v)): −0.1. [u] Ref. 20 (in THF) and ref. 21 (in CH_2Cl_2–C_6D_6 (9:1 v/v)): 222.2. [v] Ref. 21 (in CH_2Cl_2–C_6D_6 (9:1 v/v)): 11.3. [w] Ref. 21 (in CH_2Cl_2–C_6D_6 (9:1 v/v)): 230.7. [x] Ref. 25 (in CH_2Cl_2): −5.33. [y] Ref. 25 (in CH_2Cl_2): +237.

or react with itself to form a chelate ring $[W(CO)_4(P\text{-}P)]$. Both these types of complexes have been synthesized previously and their spectral (IR, NMR) properties are well documented [16–23].

Reaction of $[W(CO)_5(NCMe)]$ with the diphosphine $PPh_2(CH_2)_nPPh_2$ ($n = 2, 3$) gave no reaction at 21 °C ($CHCl_3$, MeCN, toluene) consistent with earlier reports on the reaction of $[W(CO)_5(NCMe)]$ with PPh_3 [9]. Increasing the reaction temperature to 55–65 °C did result in product formation. The reactions were terminated after 2–2½ h as at this stage no significant changes in the IR spectra could be observed. At the end of the reaction the crude or semi-purified (to remove excess diphosphine) products were analysed by IR and ^{31}P NMR spectroscopy (Table 3) and the product distribution as determined by ^{31}P NMR spectroscopy is given in Table 2. The reaction with $PMePh_2$ was also investigated and confirmed that the reaction with $[W(CO)_5NCMe)]$ only occurred at $T > 30$ °C. With the exception of the $PPh_2(CH_2)_5PPh_2$ derivatives all the compounds have been previously reported in the literature and our data are in agreement with earlier reported values [16–23].

Reactions of $PPh_2(CH_2)_nPPh_2$ ($n = 3$–5) with $[W(CO)_5(NCMe)]$ in toluene in a 1:2 ratio gave in every instance a higher amount of the bridged complex. The choice of a 1:2 ratio together with the anticipated lower bond strength of the W–NCMe (*versus* W–CO bond strength) should favour the product distribution observed [10]. Unexpectedly the use of $CHCl_3$ as solvent resulted in a change of product ratios. For the ligands $PPh_2(CH_2)_nPPh_2$ ($n = 2, 3$) the major product is still the bridged species. However for $n = 4, 5$ the major product in $CHCl_3$ is the chelate complex $[W(CO)_4(PPh_2(CH_2)_nPPh_2)]$ ($n = 4, 5$). It is difficult to reconcile this result with the known ability of diphosphines to form chelate rings containing 5 or 6 members, rather than with 7 or 8 members.

The reaction with $PPh_2CH_2PPh_2$ in a 1:1 ratio gave the expected chelate complex.

Acknowledgements

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