Oxidation of the zwitterionic tungsten amide (OC)$_5$WNPhNPhC(OMe)Ph with Br$_2$ and PCl$_5$. Formation of [(PhN)W(CO)$_2$X$_2$]$_2$ and (PhN)W(CO)$_2$X$_2$L (X = Br or Cl; L = MeCN, Me$_3$C$_6$H$_2$NH$_2$ and *i*-BuNH$_2$)

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Oxidation of the zwitterionic tungsten amide (OC)$_5$WNPhNPhC(OMe)Ph **1** with Br$_2$ or PCl$_5$ produced [(PhN)W(CO)$_2$X$_2$]$_2$ (X = Cl or Br). These halide-bridged tungsten(IV) dimers reacted with MeCN to give the mononuclear complexes (PhN)W(CO)$_2$X$_2$(MeCN) (X = Cl or Br). The latter complexes can also be obtained directly in high yield by oxidizing **1** in the presence of MeCN. The acetonitrile ligand can be substituted with Me$_3$C$_6$H$_2$NH$_2$ or *i*-BuNH$_2$ to yield (PhN)W(CO)$_2$X$_2$L (X = Cl or Br, L = Me$_3$C$_6$H$_2$NH$_2$ or *i*-BuNH$_2$) or with PMe$_3$ to produce (PhN)W(CO)Br$_2$(PMe$_3$)$_2$. The oxidation of **1** with BrI resulted in the formation of [(PhN)W(CO)$_2$Br(I)]$_2$, which reacts with MeCN to produce (PhN)W(CO)$_2$Br(I)(MeCN). The structures of the dimers [(PhN)W(CO)$_2$X$_2$]$_2$ were determined by X-ray crystallography.

Introduction

Synthetic routes involving amido ligands have become important in the preparation of imido complexes.[1] Although imido moieties can be generated in a variety of ways,[1,2] utilization of a preexisting metal–nitrogen bond is often very convenient. This strategy has proven to be particularly successful in the preparation of low-valent imido complexes, which can be difficult targets. As an example, abstraction of either a hydride or a proton has been used to generate low-valent imido complexes of the type Tp′(OC)$_2$W=NR$^+$ [Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate] from the corresponding amido complexes.[3]

We have previously reported use of the zwitterionic amido complex (OC)$_5$WNPhNPhC(OMe)Ph **1**[4] as a precursor to tungsten imido complexes in a variety of oxidation states. Cleavage of **1** under non-oxidative conditions generates the tungsten(0) complex (OC)$_5$W=NPh as a reactive intermediate,[5] while oxidation of **1** with I$_2$ produces imido complexes of W^{IV} or W^{VI}.[6] Of particular interest is the dimeric complex [(PhN)-W(CO)$_2$I$_2$]$_2$ **2** [eqn. (1)] which results from reaction of **1** with 1
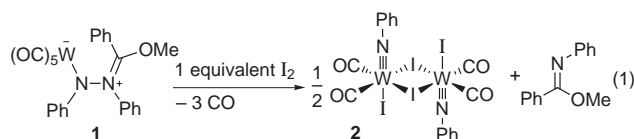
equivalent of I$_2$. Iodo-bridged dimer **2** is both a stoichiometric reagent[7a] and a catalyst[7b] for the carbonylation of primary amines to ureas. In addition, complexes of the type (PhN)-W(CO)$_2$I$_2$L, which can be produced by reaction of **2** with two-electron donor ligands L, show promise as precursors for the chemical vapor deposition of tungsten nitride thin films.[8] The exploration of these applications led us to prepare derivatives containing chloride and bromide ligands.

We now report the oxidation of zwitterion **1** with Br$_2$ or PCl$_5$ to yield the halide-bridged dimers [(PhN)W(CO)$_2$X$_2$]$_2$ (X = Cl **3** or Br **4**). In parallel with the chemistry of iodide complex **2**, derivatives of the type (PhN)W(CO)$_2$X$_2$L can be prepared from dimers **3** and **4**. In addition, when the oxidation of **1** is carried out in the presence of MeCN, the acetonitrile complexes (PhN)W(CO)$_2$X$_2$(MeCN) (X = Cl **5** or Br **6**) can be obtained

directly in more than 80% yield. The MeCN ligand can easily be substituted with amines to provide the series of complexes (PhN)W(CO)$_2$X$_2$L.

Results and discussion

Oxidation of (OC)$_5$WNPhNPhC(OMe)Ph 1 with PCl$_5$

Reaction of complex **1** with PCl$_5$ in diethyl ether at 0 °C resulted in precipitation of a red solid after about 25 min. Isolation of the solid by filtration afforded the Cl-bridged dimer **3** in 63% yield (Scheme 1). When the reaction mixture was
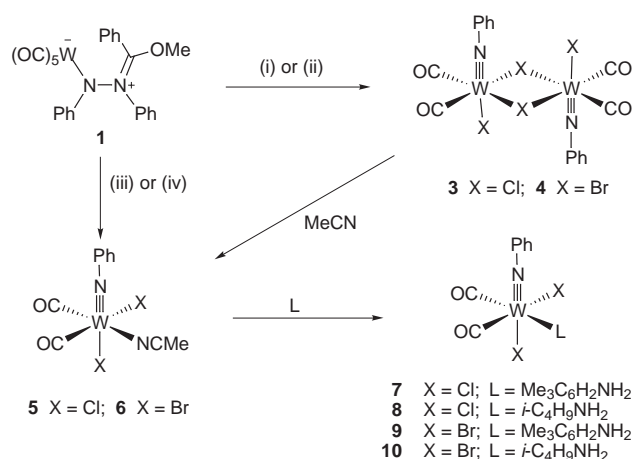
Scheme 1 (i) PCl$_5$, ether, 0 °C; (ii) Br$_2$, CH$_2$Cl$_2$, ether, −78 °C; (iii) PCl$_5$, MeCN, ether, 0 °C; (iv) Br$_2$, MeCN, ether, 0 °C.

allowed to stir for more than 3 h dimer **3** began to decompose into an insoluble blue-black solid which was not characterized. Although chlorination with PCl$_5$ was successful, reaction of **1** with Cl$_2$ did not result in formation of **3**. It is possible that the limited solubility of both PCl$_5$ and dimer **3** in ether at 0 °C allowed **3** to form and precipitate before further chlorination could occur.

Spectroscopic data for compound **3** can be found in Tables 1–3. The carbonyl bands (2084, 2016 cm^{-1}) appear at higher wavenumbers than those of its iodide analogue **2**, consistent

with the poorer electron donation from the chloride ligands *vs.* iodide. This effect is also evident in the ^{13}C NMR signals for the carbonyl carbons in dimers **2** and **3**, where the chloride dimer **3** appears downfield of iodide **2**.

Oxidation of (OC)$_5$WNPhNPhC(OMe)Ph 1 with Br$_2$ and PBr$_5$

In contrast to the well behaved reactions of compound **1** with PCl$_5$ and I$_2$, preparation of the analogous bromide dimer **4** proved problematic. When **1** was treated with 1 equivalent of Br$_2$–CH$_2$Cl$_2$ solution at -78 °C in ether containing a small amount of CH$_2$Cl$_2$ no reaction occurred initially. However, upon warming to -40 °C, the solution changed from black to dark red and a dark red sticky solid formed over the course of 2 h. The sticky solid contained dimer **4** and unstable material, which decomposed during the work-up. Purification of the crude product afforded clean **4** in 13% yield (Scheme 1). The spectroscopic data were similar to those for chloride dimer **3** and are summarized in Tables 1–3. Efforts to optimize the conditions using other solvents (CH$_2$Cl$_2$ or hexane) and altered reaction conditions were unsuccessful.

Given that the presence of an excess of I$_2$ during oxidation of compound **1** to **2** leads to overoxidation and formation of the tungsten(VI) metallacycle I$_3$(PhN)W(NPhCPhO), it seemed likely that the more strongly oxidizing Br$_2$ could also be causing overoxidation. In order to ensure low concentrations of Br$_2$, PBr$_5$ was used as a Br$_2$ equivalent. Reaction of **1** with PBr$_5$ in ether at 0 °C over 2 h afforded a red solution and a dark red sticky solid. Dimer **4** was isolated from the sticky solid in 25% yield. Once again the timing of the reaction was critical. Upon stirring the reaction mixture for 4 h dimer **4** decomposed into intractable material. Further attempts to optimize the reaction conditions using PBr$_5$ were also unsuccessful.

Oxidation of (OC)$_5$WNPhNPhC(OMe)Ph 1 with BrI

Upon addition of BrI–CH$_2$Cl$_2$ solution to an ether solution of compound **1** at room temperature immediate reaction occurred. The solution changed from black to greenish, then dark red, and red solid began to precipitate within 10 min. After 2 h of stirring a red solution containing an orange-red solid had formed. Isolation of the solid yielded the dimer [(PhN)-W(CO)$_2$Br(I)]$_2$ as the major product. As expected,[9] formation of this mixed bromide–iodide complex predominated. However, the reaction mixtures also contained trace amounts of the iodide dimer **2** and the bromide **4**, which presumably arise due to the equilibrium between BrI and Br$_2$ + I$_2$.[10] The three dimers exhibited clear differences in their solubilities, with **2** being the most soluble and **4** the least. The insolubility of **4** allowed crystals to be grown from solutions in which [(PhN)W(CO)$_2$Br(I)]$_2$ was the major component.

Crystal structures of dimers 3 and 4

The chloride- and bromide-containing complexes [(PhN)W-(CO)$_2$X$_2$]$_2$ and (PhN)W(CO)$_2$X$_2$L are rare examples of d^2 imido complexes bearing two π-acid ligands[3,6] and as such could provide insight into the problem of accommodating both strongly π-donating imido and π-acid carbonyl ligands on the same metal center. Prior studies on d^2 imido complexes bearing a single π-acid ligand have been interpreted in terms of electron donation from the imido ligand into two empty d orbitals in conjunction with back donation of the two d electrons into the empty orbitals of the π acid.[11] For compounds with multiple π acids, such as the [(PhN)W(CO)$_2$X$_2$]$_2$ and (PhN)W(CO)$_2$X$_2$L series, back donation will be affected by competition for the two d electrons. In the chloride and bromide derivatives, which will be less electron rich at the metal than iodide-containing dimer **2**, the already weak back bonding should be even less potent. This effect can be detected in the variation of carbonyl stretching frequencies as the halide is changed (Table 1). In order to see if it would also be detectable in the structures of the complexes, a crystallographic study of dimers **3** and **4** was carried out for comparison to iodide dimer **2**, whose structure was published previously.[6a]

The structures of complexes **3** and **4** appear in Figs. 1 and 2, respectively. Selected bond lengths and angles can be found in Table 4. As is also observed for iodide dimer **2**, the tungsten centers are octahedral and bear triply bonded imido ligands [W–N1 1.757(4) Å for **3**; 1.757(10) for **4**]. Within experimental error, the W–C bond lengths are the same for dimers **2** [2.051(14), 2.022(13) Å], **3** [2.043(5), 2.040(5) Å] and **4** [2.051(13), 2.029(13) Å]. The C–O bond lengths within the carbonyls are also indistinguishable in the three dimers. There is

Table 1 Infrared and ^{13}C NMR data for carbonyl ligands.

Complex	$\tilde{v}$(CO) (CH$_2$Cl$_2$)/cm^{-1}	^{13}C NMR, δ(CDCl$_3$, 20 °C)
2 [(PhN)W(CO)$_2$I$_2$]$_2$[a]	2068, 2007	202.7
4 [(PhN)W(CO)$_2$Br$_2$]$_2$	2080, 2012	208.3[b]
3 [(PhN)W(CO)$_2$Cl$_2$]$_2$	2084, 2016	210.4[b]
[(PhN)W(CO)$_2$Br(I)]$_2$	2080, 2017	207.7
(PhN)W(CO)$_2$I$_2$(MeCN)[a]	2072, 2003	206.4, 203.0
6 (PhN)W(CO)$_2$Br$_2$(MeCN)	2078, 2005	208.9, 207.1
5 (PhN)W(CO)$_2$Cl$_2$(MeCN)	2081, 2013	212.3, 210.4[b]
(PhN)W(CO)$_2$Br(I)(MeCN)	2087, 2011	207.0, 204.2
(PhN)W(CO)$_2$I$_2$(Me$_3$C$_6$H$_2$NH$_2$)[a]	2064, 1984	209.1, 207.2
9 (PhN)W(CO)$_2$Br$_2$(Me$_3$C$_6$H$_2$NH$_2$)	2076, 1995	211.9, 211.6
7 (PhN)W(CO)$_2$Cl$_2$(Me$_3$C$_6$H$_2$NH$_2$)	2087, 2011	213.7, 212.4
10 (PhN)W(CO)$_2$Br$_2$(i-C$_4$H$_9$NH$_2$)	2076, 1988	213.8, 211.3[b]
8 (PhN)W(CO)$_2$Cl$_2$(i-C$_4$H$_9$NH$_2$)	2078, 1993	216.0, 211.6
(PhN)W(CO)Br$_2$(PMe$_3$)$_2$	1953	241.9[b]

[a] Data taken from ref. 6(b). [b] Spectrum obtained in CD$_2$Cl$_2$.

Table 2 Proton and ^{13}C NMR data (δ, J/Hz) for phenyl groups.

Complex	^{1}H NMR, δ(CDCl$_3$), C$_6$H$_5$	^{13}C NMR, δ(CDCl$_3$, 20 °C)
3 *	7.48 (t, 4 H), 7.42 (m, 2 H), 7.08 (t, 4 H)	154.2, 129.4, 128.5, 125.9
5 *	7.59 (m, 1 H), 7.37 (d, $J = 8$, 2 H), 7.30 (t, 2 H)	153.9, 139.0, 129.4, 126.9
7	7.27 (m, 1 H), 7.16 (t, 2 H), 6.64 (d, $J = 8$, 2 H)	152.7, 138.0, 129.7, 126.5
8	7.34 (t, 2 H), 7.29 (m, 1 H), 7.22 (d, $J = 8$, 2 H)	153.4, 129.2, 128.8, 126.3
4	7.58 (d, $J = 8$, 4 H), 7.39 (t, 4 H), 7.23 (m, 2 H)	154.6, 130.2, 129.5, 127.8
6	7.42 (m, 1 H), 7.31 (d, $J = 7$, 2 H), 7.22 (t, 2 H)	153.5, 132.2, 129.2, 126.0
9 *	7.35 (t, 1 H), 7.18 (t, 2 H), 6.72 (d, $J = 8$, 2 H)	153.1, 138.9, 129.5, 126.3
10 *	7.44 (m, 1 H), 7.33 (t, 2 H), 7.28 (t, 2 H)	153.9, 129.7, 129.4, 126.2
(PhN)W(CO)Br$_2$(PMe$_3$)$_2$*	7.51 (m, 2 H), 7.29 (m, 1 H), 7.14 (t, 2 H)	154.9, 129.3, 127.3, 124.9
[(PhN)W(CO)$_2$Br(I)]$_2$	7.61 (m, 4 H), 7.50 (m, 2 H), 7.37 (m, 4 H)	153.8, 129.9, 129.3, 127.1
(PhN)W(CO)$_2$Br(I)(MeCN)	7.67–7.32 (m, 5 H)	153.4, 129.1, 126.0, 125.6

* Spectrum obtained in CD$_2$Cl$_2$.

Table 3 Proton and ^{13}C NMR data (δ, J/Hz) for ancillary ligands.

| | | $\delta(CDCl_3$, 20 °C) | |
Complex	Ligand	^1H NMR	^{13}C NMR
5[a]	MeCN	2.68 (s, 3 H, CH$_3$CN)	129.2, (CH$_3$CN), 4.7 (CH$_3$CN)
7	NH$_2$C$_6$H$_2$Me$_3$	6.81 (s, 2 H, C$_6$H$_2$)	135.1, 128.8, 128.6, 127.1 (C$_6$H$_2$), 20.5, 18.0 (CH$_3$C$_6$H$_2$)
		6.30 (d, J = 12, 1 H, NH$_2$)	
		5.57 (d, J = 12, 1 H, NH$_2$)	
		2.42 (s, 6 H, CH$_3$)	
		2.28 (s, 3 H, CH$_3$)	
8	MeCHCH$_2$Me	4.23 (dd, 1 H, NH$_2$)	56.5 (H$_2$NCH)
	|	3.77 (dd, 1 H, NH$_2$)	31.7 (H$_2$NCHCH$_3$)
	NH$_2$	3.33 (m, 1 H, CH)	21.5 (H$_2$NCHCH$_2$)
		1.64 (m, 2 H, CH$_2$)	10.0 (CHCH$_2$CH$_3$)
		1.33 (t, 3 H, CH$_3$)	
		0.99 (t, 3 H, CH$_3$)	
6	MeCN	2.75 (s, 3 H, CH$_3$CN)	125.3 (CH$_3$CN), 5.1 (CH$_3$CN)
9	NH$_2$C$_6$H$_2$Me$_3$	6.85 (s, 2 H, C$_6$H$_2$)	135.7, 130.1, 129.9, 129.2 (C$_6$H$_2$), 20.6, 18.5 (CH$_3$C$_6$H$_2$)
		6.32 (d, J = 11, 1 H, NH$_2$)	
		5.55 (d, J = 12, 1 H, NH$_2$)	
		2.42 (s, 6 H, CH$_3$C$_6$H$_2$)	
		2.26 (s, 3 H, CH$_3$C$_6$H$_2$)[a]	
10[a]	MeCHCH$_2$Me	4.27 (dd, 1 H, NH$_2$)	57.8 (H$_2$NCH)
	|	3.88 (dd, 1 H, NH$_2$)	32.1 (H$_2$NCHCH$_3$)
	NH$_2$	3.38 (m, 1 H, CH)	21.7 (H$_2$NCHCH$_2$)
		1.64 (m, 2 H, CH$_2$)	10.2 (CHCH$_2$CH$_3$)
		1.32 (t, 3 H, CH$_3$)	
		1.00 (t, 3 H, CH$_3$)	
a,b	PMe$_3$	1.74 (t, 18 H, PMe$_3$)	16.4 [t, P(CH$_3$)$_3$]
c	MeCN	2.78 (s, 3 H, CH$_3$CN)	124.9 (CH$_3$CN), 4.9 (CH$_3$CN)

[a] Spectrum obtained in CD$_2$Cl$_2$. [b] Complex (PhN)W(CO)Br$_2$(PMe$_3$)$_2$: ^{31}P NMR (CD$_2$Cl$_2$) δ −26.0 (t, J_{WP} = 285.0 Hz, PMe$_3$). [c] (PhN)W(CO)$_2$-Br(I)(MeCN).
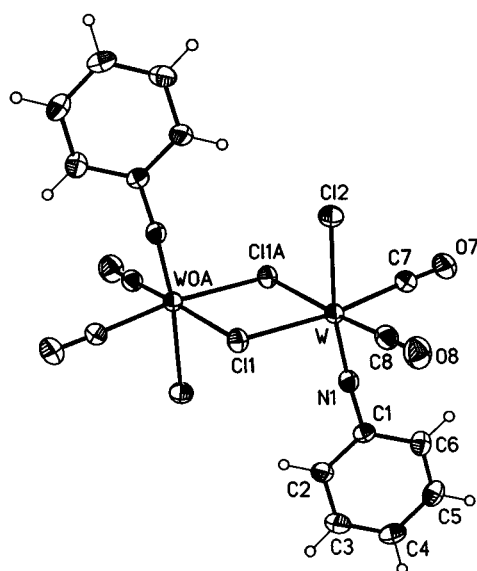
Fig. 1 Thermal ellipsoid diagram of [(PhN)W(CO)$_2$Cl$_2$]$_2$ **3** showing the crystallographic numbering scheme.

Fig. 2 Thermal ellipsoid diagram [(PhN)W(CO)$_2$Br$_2$]$_2$ **4** showing the crystallographic numbering scheme.

thus no structural evidence for variation in the back bonding to the carbonyl ligands as the halide ligands are changed. The W–X bond distances in **3** [terminal 2.4349(12); bridging 2.4991(12) Å] and **4** [terminal 2.6729(13); bridging 2.7204(11) Å] fall within the normal ranges.[12] The structural differences in the W$_2$X$_2$ cores of the dimers can be attributed to the variation in W–X bond lengths as X is varied.

Reactions of dimers 3, 4 and [(PhN)W(CO)$_2$Br(I)]$_2$ with donor ligands

When dimers **3** and **4** are dissolved in MeCN dissociation and solvent co-ordination result in formation of the acetonitrile complexes (PhN)W(CO)$_2$Cl$_2$(MeCN) **5** and (PhN)W(CO)$_2$Br$_2$-

(MeCN) **6**, respectively. Similar behavior has been reported for iodide dimer **2**.[6] Reaction of the mixed bromide–iodide dimer [(PhN)W(CO)$_2$Br(I)]$_2$ with MeCN overnight yielded only the mixed halide complex (PhN)W(CO)$_2$Br(I)(Me$_3$CN). Neither (PhN)W(CO)$_2$I$_2$(MeCN) nor (PhN)W(CO)$_2$Br$_2$(MeCN) **6** were produced from [(PhN)W(CO)$_2$Br(I)]$_2$. This result suggests that the bridging halides in the latter are either both iodide or both bromide. We have no experimental evidence to distinguish between the possibilities, as X-ray quality crystals could not be obtained. However, the precedent from molecules such as [Mo(μ-I)Br(CO)$_3$(PPh$_3$)]$_2$[9] suggests that iodide bridging would be preferred.

Reaction of bromide dimer **4** with an excess of PMe$_3$ in CH$_2$Cl$_2$ results in formation of the bis(PMe$_3$) complex (PhN)-

Table 4 Selected bond lengths (Å) and angles (°) for complexes **3** and **4**.

Complex **3**		Complex **4**	
W–N1	1.757(4)	W–N1	1.757(10)
W–C7	2.043(5)	W–C7	2.051(13)
W–C8	2.040(5)	W–C8	2.029(13)
W–Cl2	2.4349(12)	W–Br2	2.6729(13)
W–Cl1	2.4991(12)	W–Br1	2.7204(11)
W–Cl1A	2.5085(12)	W–Br1A	2.7318(11)
N1–Cl	1.387(6)	N1–Cl	1.37(2)
C7–O8	1.131(7)	O7–C7	1.12(2)
C8–O8	1.125(7)	O8–C8	1.14(2)
N1–W–C8	89.3(2)	N1–W–C8	91.4(5)
N1–W–C7	90.0(2)	N1–W–C7	91.3(5)
C7–W–C8	89.0(2)	C8–W–C7	89.3(5)
N1–W–Cl2	170.99(13)	N1–W–Br2	170.2(3)
C8–W–Cl2	83.8(2)	C8–W–Br2	81.4(4)
C7–W–Cl2	84.2(2)	C7–W–Br2	82.1(4)
N1–W–Cl1	96.77(13)	N1–W–Br1	96.8(3)
C8–W–Cl1	94.4(2)	C8–W–Br1	93.2(4)
C7–W–Cl1	172.5(2)	C7–W–Br1	171.5(4)
Cl2–W–Cl1	89.54(4)	Br2–W–Br1	90.25(4)
N1–W–Cl1A	98.65(13)	N1–W–Br1A	98.3(3)
C8–W–Cl1A	170.92(14)	C8–W–Br1A	169.9(4)
C7–W–Cl1A	95.3(2)	C7–W–Br1A	93.2(4)
Cl2–W–Cl1A	88.72(4)	Br2–W–Br1A	89.26(4)
Cl1–W–Cl1A	80.35(4)	Br1–W–Br1A	82.92(3)
W–Cl1–W0A	99.65(4)	W–Br1–W0A	97.08(3)
C1–N1–W	174.9(3)	C1–N1–W	177.1(9)
N1–C1–C2	118.5(4)	N1–C1–C2	120.0(12)
N1–C1–C6	120.3(4)	N1–C1–C6	119.2(11)
O8–C8–W	178.4(5)	O7–C7–W	177.0(13)
O7–C7–W	178.0(5)	O8–C8–W	177.3(13)

$W(CO)Br_2(PMe_3)_2$. As is also observed for the chemistry of iodide dimer **2**,[6] one of the CO ligands is replaced by the more strongly nucleophilic PMe_3. The ^{31}P NMR spectrum exhibits a signal at $\delta -26.0$ for PMe_3. The signal is shifted downfield with respect to its iodide analogue $(PhN)W(CO)I_2(PMe_3)_2$ ($\delta -38.8$) as expected for the more electron poor bromide complex.

Oxidation of $(OC)_5WNPhNPhC(OMe)Ph$ 1 with Br_2 and PCl_5 in the presence of MeCN

Although acetonitrile complexes **5** and **6** are accessible *via* reaction of dimers **3** and **4** with MeCN, poor yields during the dimer syntheses result in low overall yields for **5** and **6**. Therefore, more direct routes to them were developed. Oxidation of zwitterion **1** with Br_2 in the presence of MeCN at $-78\,^{\circ}C$ resulted in formation of a red solution containing a red precipitate of MeCN complex **6**. Simple filtration and washing of the solid afforded 81% yield. A similar protocol involving oxidation of **1** with PCl_5 in the presence of MeCN at $0\,^{\circ}C$ produced complex **5** in 88% yield. Clearly, the yields of MeCN complexes obtained upon oxidation in the presence of a co-ordinating solvent are much higher than the yields of dimer obtained in non-co-ordinating solvents. This effect can be attributed to trapping of the unsaturated intermediate $[X_2(OC)_2W(NPh)]$ before side reactions can compete with dimerization.

Substitution of the MeCN ligand in $(PhN)W(CO)_2X_2(MeCN)$ with $Me_3C_6H_2NH_2$ and *i*-BuNH$_2$

Since MeCN complexes **5** and **6** were readily available we explored substitution of the acetonitrile ligand as a means of generating derivatives. The hindered arylamine 2,4,6-Me_3C_6-H_2NH_2 had been demonstrated to serve as a ligand in the iodide system, where the amine was treated with dimer **2** to generate $(PhN)W(CO)_2I_2(Me_3C_6H_2NH_2)$.[6b] Treatment of **5** and **6** with 1 equivalent of $Me_3C_6H_2NH_2$ in CH_2Cl_2 solution results in the

formation of the $Me_3C_6H_2NH_2$ complexes **7** and **9** (Scheme 1) within 2 h. The IR spectrum of **9** exhibited two CO bands at 2076 and 1995 cm^{-1}, while the two CO bands for **7** appeared at 2087 and 2011 cm^{-1}. These values are higher than the corresponding 2064 and 1984 cm^{-1} for the iodide derivative, consistent with the weakening of electron donation to the metal upon proceeding from iodide to bromide to chloride.

Similarly, reaction of compounds **5** and **6** with 1 equivalent of *i*-BuNH$_2$ in CH_2Cl_2 solution yielded the *i*-BuNH$_2$ complexes **8** and **10**. Owing to the chirality of the metal center and the amine a mixture of diastereomers was obtained. This was reflected in the ^1H NMR spectra, which exhibited broad multiplets at δ 1.64 for the CH_2 group next to the chiral carbon. In addition the ^{13}C NMR spectra contained two sets of carbon signals for the isobutyl groups of the diastereomers. The reported data (Tables 1–3) correspond to the major isomers.

Conclusion

Oxidation of the zwitterionic amide complex $(OC)_5WNPh$-$PhC(OMe)Ph$ **1** with Br_2 and PCl_5 at low temperature in ether solution results in formation of the dimeric complexes $[(PhN)$-$W(CO)_2X_2]_2$ (X = Cl; **3** or Br **4**). These dimers are congeners of the previously reported iodo-bridged dimer **2**, but are more reactive than it due to the poorer bridging ability of Br and Cl. Reaction of them with two-electron donor ligands L produces complexes of the type $(PhN)W(CO)_2X_2L$. When oxidation of **1** with Br_2 and PCl_5 is conducted in the presence of the co-ordinating solvent MeCN, the mononuclear complexes $(PhN)W(CO)_2X_2(MeCN)$ (X = Cl **5** or Br **6**) are obtained directly in more than 80% yield. The MeCN ligand in complexes **5** and **6** can easily be replaced with amines such as $Me_3C_6H_2NH_2$ and *i*-BuNH$_2$.

Experimental

General

Standard inert atmosphere techniques were used throughout. Hexane, acetonitrile and methylene chloride were distilled from CaH_2, diethyl ether and THF from Na/Ph_2CO. The NMR solvents were degassed by three freeze–pump–thaw cycles and stored over 3 Å molecular sieves in a dry-box. Iodine mono-bromide was purchased from Aldrich as a 1.0 M solution in CH_2Cl_2 and used as received. All other reagents were purchased in reagent grade and used without further purification. The ^1H, ^{13}C and ^{31}P NMR spectra were recorded on Gemini-300 or VXR-300 spectrometers, IR spectra on a Perkin-Elmer 1600 spectrometer. High resolution mass spectrometry was performed by the University of Florida analytical service. Elemental analyses were performed by Robertson Microlit Laboratories, Madison, NJ.

Syntheses

$[(PhN)W(CO)_2Cl_2]_2$ 3. Zwitterion **1** (1.3 g, 2.1 mmol) and PCl_5 (432.5 mg, 2.08 mmol) were placed in a Schlenk vessel and cooled to $0\,^{\circ}C$. Diethyl ether (25 mL) and 4 mL of CH_2Cl_2 were added *via* syringe. After 25 min a red solid began to form. The solution was stirred at $0\,^{\circ}C$ for 1.5 h. The solvent was removed by cannulation and the solid washed with ether (5 mL × 3) to yield complex **3** as an orange-red solid. Yield 524 mg, 62.7% (Found: C, 23.62; H, 1.29; N, 3.75. Calc. for $C_8H_5Cl_2NO_2W$: C, 23.91; H, 1.25; N, 3.48%).

$(PhN)W(CO)_2Cl_2(MeCN)$ 5. Zwitterion **1** (1.37 g, 2.19 mmol) and PCl_5 (456 mg, 2.19 mmol) were placed in a Schlenk vessel and cooled to $0\,^{\circ}C$. Ether (15 mL) was added, then 3 mL of MeCN were added within 5 min. A vigorous reaction occurred upon addition of MeCN, as evidenced by a change

from black to dark red. The reaction mixture was stirred for 1.5 h at 0 °C followed by 0.5 h at room temperature, during which a purple-red solid formed. The solvent was removed by cannulation and the solid washed with ether (5 mL × 3) to yield complex **5** as a purple-red solid. Yield 852 mg, 87.8% (Found: C, 27.28; H, 1.67; N, 6.19. Calc. for $C_{10}H_8Cl_2N_2W$: C, 27.12; H, 1.82; N, 6.33%).

(PhN)W(CO)$_2$Cl$_2$(Me$_3$C$_6$H$_2$NH$_2$) 7. Complex **5** (317 mg, 0.59 mmol) was dissolved in 8 mL of CH_2Cl_2 and $Me_3C_6H_2NH_2$ (105.5 µL, 0.59 mmol) was added *via* syringe. The solution was stirred at room temperature for 2 h, during which the solution changed from purple-red to bright red. The solvent was removed under vacuum and the residue extracted with 10 mL of ether. Removal of the ether *via* vacuum yielded pure **7** as a red powder. Yield 282 mg, 89% (Found: C, 38.31; H, 3.49; N, 5.16. Calc. for $C_{17}H_{18}Cl_2N_2O_2W$: C, 38.02; H, 3.38; N, 5.22%).

(PhN)W(CO)$_2$Cl$_2$(i-C$_4$H$_9$NH$_2$) 8. Complex **5** (237.5 mg, 0.54 mmol) was dissolved in 8 mL of CH_2Cl_2 and i-$C_4H_9NH_2$ (56 µL, 0.54 mmol) was added *via* syringe. The solution was stirred for 2 h, then the solvent was removed under vacuum. The residue was extracted with ether–hexane (5 : 1) to yield a red solution from which complex **8** was obtained as a red powder upon evaporation of the solvent. Yield 184 mg, 71.7% (Found: C, 30.57; H, 3.64; N, 6.13. Calc. for $C_{12}H_{16}Cl_2N_2O_2W$: C, 30.34; H, 3.40; N, 5.90%).

[(PhN)W(CO)$_2$Br$_2$]$_2$ 4. Zwitterion **1** (1.95 g, 3.12 mmol) was dissolved in 100 mL of ether and cooled to −78 °C, after which a solution of Br_2 in CH_2Cl_2 (499 mg, 3.12 mmol in 6 mL of CH_2Cl_2) was added *via* syringe. The solution was stirred for 2 h while the temperature was allowed to rise from −78 to −20 °C. During this period some dark red sticky solid formed and the solution changed from black to red. The reaction was allowed to continue for 0.5 h at room temperature and the ether was then removed by cannulation. The sticky solid was recrystallized with CH_2Cl_2–ether (1 : 3 by volume). The mother liquor was separated and the solvent removed from it by evaporation. The residue was then washed with ether to yield dimer **4** as a red solid. Yield 205 mg, 13.4% (Found: C, 19.47; H, 1.03; N, 2.81. Calc. for $C_8H_5Br_2NO_2W$: C, 19.58; H, 1.03; N, 2.85%).

(PhN)W(CO)$_2$Br$_2$(MeCN) 6. Zwitterion **1** (1.20 g, 1.92 mmol) was dissolved in 15 mL of ether and cooled to −78 °C. A solution of Br_2 in CH_2Cl_2 (307 mg, 1.92 mmol in 4 mL of CH_2Cl_2) was added *via* syringe, then 2 mL of MeCN were introduced. Within 10 min the solution changed from black to red and red solid began to form. The solution was stirred for 2 h while the temperature rose from −78 °C to room temperature and then was stirred for 0.5 h at room temperature. The solvent was removed by cannulation and the solid washed with ether (2 × 5 mL) to yield complex **6** as a dark red solid. Yield 830 mg, 81.3%. HRMS (FAB): (M − CO)$^+$, found 503.8535, calc. 503.8479.

(PhN)W(CO)$_2$Br$_2$(Me$_3$C$_6$H$_2$NH$_2$) 9. Complex **6** (81 mg, 0.15 mmol) was dissolved in 8 mL of CH_2Cl_2 and $Me_3C_6H_2NH_2$ (22.5 µL, 0.15 mmol) added *via* syringe. The solution was stirred for 1 h, during which it changed from dark red to bright red. The solvent was removed under vacuum and the residue extracted with ether. Removal of the ether yielded complex **9** as a red powder. Yield 54 mg, 57.5% (Found: C, 32.57; H, 2.65; N, 4.53. Calc. for $C_{17}H_{18}Br_2N_2O_2W$: C, 32.62; H, 2.90; N, 4.48%).

(PhN)W(CO)$_2$Br$_2$(i-C$_4$H$_9$NH$_2$) 10. Complex **6** (71 mg, 0.13 mmol) was dissolved in 10 mL of CH_2Cl_2 and i-$C_4H_9NH_2$ (13.70 µL, 0.13 mmol) added *via* syringe. The solution was stirred at room temperature for 2 h, during which a bright red color developed. The solvent was removed under vacuum and

the residue extracted with 15 mL of ether. Removal of the ether yielded complex **10** as a sticky red solid. Yield 44 mg, 60.0%. HRMS (FAB): (M − 2CO)$^+$, found 507.9343, calc. 507.9174.

(PhN)W(CO)Br$_2$(PMe$_3$)$_2$. Dimer **4** (320 mg, 0.33 mmol) was dissolved in 10 mL of CH_2Cl_2 and PMe$_3$ (5 equivalents) was added *via* syringe. The solution was stirred at room temperature for 2 h, then the solvent was removed and the residue extracted with ether–hexane (2 : 1). Removal of the solvent yielded the complex as a purple-red solid. Yield 280 mg, 64.0%. HRMS (FAB): (M − CO)$^+$, found 586.9229, calc. 586.9167.

[(PhN)W(CO)$_2$Br(I)]$_2$. Zwitterion **1** (2.0 g, 3.20 mmol) was dissolved in 15 mL of ether at 0 °C and BrI–CH_2Cl_2 solution (3.20 mL, 1.0 M in CH_2Cl_2) was added *via* syringe. Reaction occurred immediately as evidenced by a change from black to red and the dimer began to precipitate as an orange red solid. The solution was stirred for 2 h and the solvent then removed by cannulation. The resulting solid was washed with ether (2 mL × 3) to yield an orange-red solid. Yield 980 mg, 57% (Found: C, 17.83; H, 1.08; N, 2.43. Calc. for $C_8H_5BrINO_2W$: C, 17.87; H, 0.94; N, 2.61%).

(PhN)W(CO)$_2$Br(I)(MeCN). The above dimer (432 mg, 0.40 mmol) was dissolved in 10 mL of MeCN and the solution was stirred at room temperature overnight, during which it became dark red. The solvent was removed under vacuum and the residue recrystallized with CH_2Cl_2–hexane to yield the complex as a red solid. Yield 252 mg, 54.4%. HRMS (FAB): (M − CO)$^+$, found, 549.8339, calc. 549.8355.

X-Ray crystallography

Crystals of complex **4** were obtained by slow recrystallization in CH_2Cl_2–toluene (60 : 1) at −20 °C. Crystals of complex **3** were obtained from CH_2Cl_2–toluene (20 : 1) under similar conditions. Data for both compounds were collected at 173 K on a Siemens CCD SMART PLATFORM equipped with a CCD area detector and a graphite monochromator utilizing Mo-Kα radiation ($\lambda = 0.71073$ Å). Cell parameters were refined using 6121 and 5919 reflections from the bromo dimer **4** and chloro dimer **3** data sets, respectively. A hemisphere of data (1381 frames) was collected using the ω-scan method (0.3° frame width). The first 50 frames were remeasured at the end of data collection to monitor instrument and crystal stability (maximum correction on *I* was <1%). Absorption corrections were applied based on the ψ scan using the entire data sets.

Table 5 Crystallographic data for complexes **3** and **4*****

	3	**4**
Empirical formula	$C_{16}H_{10}Cl_4N_2O_4W$	$C_{16}H_{10}Br_4N_2O_4W_2$
M	803.76	981.60
a/Å	7.1433(3)	7.1118(1)
b/Å	10.1298(4)	10.4920(1)
c/Å	14.9460(7)	15.7374(1)
β/°	95.139(1)	95.079(1)
V/Å^3	1077.15(8)	1169.66(2)
Total reflections measured	7669	8334
Unique reflections	2475	2685
μ(Mo-Kα)/mm^{-1}	11.191	16.682
Goodness of fit S	1.13	1.12
R1/Reflections [$I > 2\sigma(I)$]	3.10/2334	4.90/2423
wR2/Reflections	6.75/2475	12.53/2685
Minimum, maximum peaks in Fourier-difference map/ e Å^{-3}	−1.48, 0.98	−1.90, 2.67

* Details in common: monoclinic, space group $P2_1/n$; $Z = 2$; R1 = $\Sigma(||F_o| − |F_c||)/\Sigma|F_o|$; wR2 = $[\Sigma w(F_o^2 − F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$; $S = [\Sigma w(F_o^2 − F_c^2)^2/(n − p)]^{\frac{1}{2}}$, n = number of reflections, p = number of parameters refined; $w = 1/[\sigma^2(F_o^2) + (0.0370p)^2 + 0.31p]$, $p = [\max(F_o^2,0) + 2F_c^2]/3$.

Both structures were solved by direct methods in SHELXL 97,[13] and refined using full-matrix least squares on F^2. The non-H atoms were refined with anisotropic thermal parameters. All of the H atoms were included in the final cycle of refinement riding on the atoms to which they are bonded. A total of 128 parameters were refined in the final cycle of refinement of each compound using 2423 and 2334 reflections for **4** and **3**, respectively, with $I > 2\sigma(I)$ to yield $R1$ and $wR2$ of 0.049 and 0.1253 for **4** and 0.031 and 0.067 for **3**. Crystallographic data are given in Table 5.

CCDC number 186/1110.

See http://www.rsc.org/suppdata/dt/1998/3373/ for crystallographic files in .cif format.

References

1 D. E. Wigley, *Prog. Inorg. Chem.*, 1994, **42**, 239.
2 W. A. Nugent and B. L. Haymore, *Coord. Chem. Rev.*, 1980, **31**, 123; S. Cenini and G. La Monica, *Inorg. Chim. Acta*, 1976, **18**, 279.
3 L. W. Francisco, P. S. White and J. L. Templeton, *Organometallics*, 1997, **16**, 2547; S. G. Feng, P. S. White and J. L. Templeton, *Organometallics*, 1995, **14**, 5184; P. J. Pérez, P. S. White, M. Brookhart and J. L Templeton, *Inorg. Chem.*, 1994, **33**, 6050; K. R. Powell, P. J. Pérez, L. Luan, S. G. Feng, P. S. White, M. Brookhart and J. L Templeton, *Organometallics*, 1994, **13**, 1851; L. Luan, M. Brookhart and J. L. Templeton, *Organometallics*, 1992, **11**, 1433; P. J. Pérez, L. Luan, P. S. White, M. Brookhart and J. L. Templeton, *J. Am. Chem. Soc.*, 1992, **114**, 7928; L. Luan, P. S. White, M. Brookhart and J. L. Templeton, *J. Am. Chem. Soc.*, 1990, **112**, 8190.
4 S. T. Massey, N. D. R. Barnett, K. A. Abboud and L. McElwee-White, *Organometallics*, 1996, **15**, 4625.
5 C. T. Maxey, H. F. Sleiman, S. T. Massey and L. McElwee-White, *J. Am. Chem. Soc.*, 1992, **114**, 5153; B. A. Arndtsen, H. F. Sleiman, A. K. Chang and L. McElwee-White, *J. Am. Chem. Soc.*, 1991, **113**, 4871; H. F. Sleiman, S. Mercer and L. McElwee-White, *J. Am. Chem. Soc.*, 1989, **111**, 8007; H. F. Sleiman and L. McElwee-White, *J. Am. Chem. Soc.*, 1988, **110**, 8700.
6 (*a*) P. C. McGowan, S. T. Massey, K. A. Abboud and L. McElwee-White, *J. Am. Chem. Soc.*, 1994, **116**, 7419; (*b*) N. D. R. Barnett, S. T. Massey, P. C. McGowan, J. J. Wild, K. A. Abboud and L. McElwee-White, *Organometallics*, 1996, **15**, 424.
7 (*a*) J. E. McCusker, K. A. Abboud and L. McElwee-White, *Organometallics*, 1997, **16**, 3863; (*b*) J. E. McCusker, J. Logan and L. McElwee-White, *Organometallics*, in press.
8 S. W. Johnston, Y.-X. He, T. J. Anderson and L. McElwee-White, unpublished work.
9 P. K. Baker, K. R. Flower, H. M. Naylor and K. Voigt, *Polyhedron*, 1993, **12**, 357.
10 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th edn., Wiley-Interscience, New York, 1988, pp. 570–572.
11 F.-M. Su, J. C. Bryan, S. Jang and J. M. Mayer, *Polyhedron*, 1989, **8**, 1261.
12 A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson and R. Taylor, *J. Chem. Soc., Dalton Trans.*, 1989, S1.
13 G. M. Sheldrick, SHELXL 97, Program for the refinement of crystal structures. University of Göttingen, 1997.

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