Oxidation of the Zwitterion (CO)₅WNPhNPhC(OMe)Ph with I₂. Formation of Tungsten(IV) Imido Complexes and a Tungsten(VI) Metallacycle

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Reaction of the zwitterion $(CO)_5WNPhNPhC(OMe)Ph$ (**1**) with 1 equiv of I_2 produces the iodo-bridged imido dimer $[(CO)_2W(NPh)I_2]_2$ (**2**) and the imidate $PhN=C(OMe)Ph$. Oxidation of **1** with 2 equiv of I_2, however, leads to the formation of the unusual 16-electron tungsten(VI) metallacycle $I_3(PhN)WNPhCPhO$ (**8**). The structure of **8** was determined by X-ray crystallography. Mechanistic studies on the formation of both **2** and **8** are consistent with initial iodination of the metal center of **1**, followed by N–N bond cleavage to form $(CO)_3W(NPh)I_2$ as a common intermediate. Loss of a labile CO ligand and dimerization produces **2**, while further oxidation with a second equivalent of I_2 and reaction with the side product $PhN=C(OMe)Ph$ leads to **8** and MeI. Treatment of dimer **2** with two-electron-donor ligands results in the formation of compounds of the type $(CO)_2I_2W(NPh)L$, where $L = THF$, CH_3CN, pyridine, NEt_3, or $2,4,6-Me_3C_6H_2NH_2$.

Introduction

Interaction of the strong π-donor ligand [NR]²⁻ with π-acidic ligands such as CO, CNR, olefins, and acetylenes on a single metal center has been the focus of a number of studies. To date, isolable metal imido complexes of this type have been restricted to d² species with one[1–6] and, in rare instances, two π-acidic ligands.[7,8] Theoretical arguments based on the structural and spectroscopic properties of stable complexes indicate that both types of ligands are supported by a d² electron configuration where two empty d orbitals are available for π-interactions with the [NR]²⁻ moiety and one filled d orbital participates in back-donation to the π-acceptor ligand(s). When only a single π-acceptor is present, back-donation from the filled d orbital is appreciable. The high barriers to rotation of coordinated acetylene and olefin ligands as well as the low carbonyl stretching frequency in d² imido complexes testify to the strength of this interaction. However, in high-valent imido complexes with multiple π-acids, back-donation from the filled metal d orbital is significantly diminished due to competition. This is evidenced by the high carbonyl stretching frequencies found in tungsten(IV) complexes containing the (RN)W(CO)₂ fragment.[7,8]

We recently reported the synthesis and characterization of several tungsten(IV) imido complexes that contain one and two carbonyl ligands.[8] These compounds were prepared by oxidation of the zwitterion $(CO)_5$-$WNPhNPhC(OMe)Ph$ (**1**) with 1 equiv of I_2. In this reaction, **1** serves as a protected form of the low-valent imido complex $(CO)_5W=NPh$. Since the precursor already contains five carbonyl ligands, the synthetic difficulties of introducing multiple π-acid ligands into a higher valent system are avoided. We now report the extension of this strategy to the preparation of additional compounds of the type $(CO)_2I_2W(NPh)L$. In addition, we report further oxidation of **1** to the tungsten(VI) metallacycle $I_3(PhN)WNPhCPhO$.

Results and Discussion

Treatment of a methylene chloride solution of the zwitterion $(CO)_5WNPhNPhC(OMe)Ph$ (**1**) with 1 equiv of I_2 results in immediate effervescence as the solution turns from black to green. Over the course of 30 min, the green solution becomes red and the iodo-bridged tungsten(IV) imido dimer $[(CO)_2W(NPh)I_2]_2$ (**2**) can be isolated (eq 1). This reaction is formally equivalent to

$$(1)$$
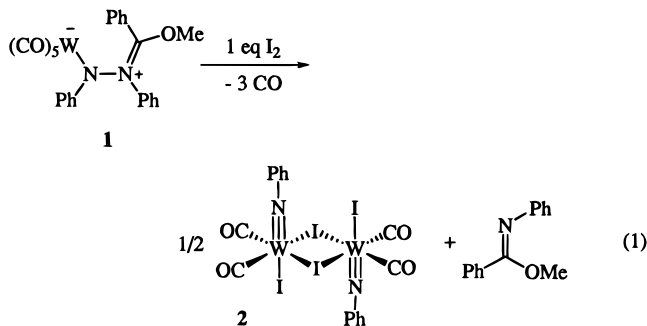
oxidation of the transient zero-valent nitrene complex $(CO)_5W=NPh$, a species that is invoked in the thermal

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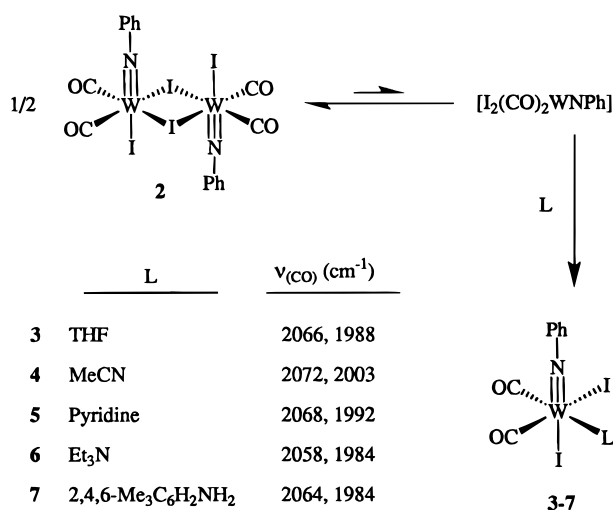(4) Johnson, L. K.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 8130–8145.
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Scheme 1

	L	$\nu_{(CO)}$ (cm^{-1})
3	THF	2066, 1988
4	MeCN	2072, 2003
5	Pyridine	2068, 1992
6	Et$_3$N	2058, 1984
7	2,4,6-Me$_3$C$_6$H$_2$NH$_2$	2064, 1984

decomposition of (CO)$_5$WNPhNPhC(OMe)R (R = Me, Ph (**1**)).[9] However, the first step of the oxidation reaction cannot be the N–N bond cleavage of **1** to give PhN=C(OMe)Ph and (CO)$_5$W=NPh, since thermal decomposition of **1** occurs over several hours in the absence of oxidizing agents, whereas the reaction between **1** and I$_2$ is complete in less than 5 s. Thus, oxidation of the W(0) center of zwitterion **1** must be followed by rapid N–N bond cleavage. The zwitterionic ligand of **1** may be regarded as a protected imido functionality that is unmasked *in situ* upon oxidation of the metal center. Since oxidation of the metal center in **1** occurs *before* N–N bond cleavage, the imido ligand is generated in a higher valent complex that is more compatible with its strongly donating nature.

The moderate yield of **2** originally reported[8] (42% based on **1**) reflects difficulty in purifying the product, rather than low conversion of **1** to **2**. In a modification of the previously described experimental procedure, a significant improvement in the yield of **2** is achieved if the reaction is carried out in diethyl ether. Over a period of 1 h, dimer **2** precipitates as a bright red powder while the PhN=C(OMe)Ph byproduct remains in solution. Filtering the reaction mixture followed by washing with Et$_2$O results in pure **2** in 76.5% yield.

The enhanced yield of dimer **2** from the simplified synthetic procedure has enabled the preparation of **2** on a multigram scale. Dimer **2** is thus a synthetically viable precursor to a series of mononuclear W(IV) imido complexes. Addition of Lewis bases to **2** results in the replacement of the weak iodide bridges to give complexes of the type (CO)$_2$I$_2$LWNPh (Scheme 1). When

the red dimer is dissolved in THF, a green solution results. Removal of the solvent gives a green oil, which was characterized as the THF adduct **3**. Due to the lability of the THF ligand, **3** could not be obtained in pure form. Samples contained free THF and some dimer **2** as an impurity. Under vacuum, complex **3** loses THF and reverts to **2**. Dimer **2** could also be quantitatively converted to acetonitrile complex **4**. Initially, dimer **2** does not dissolve in acetonitrile. However, after 30 min of stirring, all of the dimer is consumed. The acetonitrile ligand in complex **4** did not prove to be so labile, and the complex could be cleanly isolated as a solid. Syntheses of **5** and **6** in high yields are representative of the reaction between dimer **2** and tertiary amines. However, isolating the adducts of primary and secondary amines has proven problematic. Large amounts of the HI salt of the amine are often observed, indicating that decomposition of the amine adduct through loss of HI is occurring. In addition, many of the adducts are oils that do not survive column chromatography, making purification difficult. Despite the complications that arise from the reactions of primary and secondary amines with **2**, the highly hindered amine 2,4,6-Me$_3$C$_6$H$_2$NH$_2$ produced an adduct (**7**) that could be easily isolated as a solid in high yield.

The ^{13}C NMR spectra of mononuclear complexes **3**–**7** each exhibit two inequivalent carbonyl signals,[10] allowing the assignment of the carbonyl ligands as *cis*. In the case of **5**, where L = pyridine, a crystal structure analysis has confirmed that both carbonyls are also *cis* to the imido ligand.[11] The ^{1}H NMR spectra of the adducts **3**, **6**, and **7**, respectively, reflect the chirality of the metal center as the β-hydrogens of the THF and triethylamine ligands and the amine protons in the 2,4,6-Me$_3$C$_6$H$_2$NH$_2$ ligand are diastereotopic. The β-hydrogens of the THF ligand are a well-resolved, complex multiplet at 4.73 ppm, and the triethylamine β-hydrogens are a doublet of quartets at 3.38 ppm. The diastereotopic NH protons of the amine ligand in **7** are seen as doublets at 6.44 and 5.51 ppm with a coupling of 4 Hz.

The imido dimer **2** and complexes **3**–**7** belong to an unusual class of transition-metal complexes that possess both strong π-donor and π-acceptor ligands. Since the imido ligand is a hard base, it prefers the empty, low-lying d orbitals found in high-valent metal systems for donation of electron density. However, soft π-acids such as carbonyl ligands prefer the filled, diffuse metal d orbitals found in low-valent metals for effective d$_\pi$–p$_\pi$ back-donation. Competition between the two carbonyl ligands for available electrons on the d^2 metal center is reflected in the IR spectrum, where high carbonyl stretching frequencies are found in complexes of the type Tp′W(CO)$_2$(NR)$^+$,[7] imido dimer **2**, and monomers **3**–**7** (Scheme 1). To date, these are the only complexes of this type that have been fully characterized.

Oxidation of Zwitterion 1 with 2 Equiv of I$_2$. In contrast to the reaction between zwitterion **1** and 1 equiv of I$_2$, oxidation of **1** with 2 equiv of I$_2$ eventually results in a blue solution from which dark metallic blue

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(10) Only a single resonance for the carbonyls of **6** could be found in its ^{13}C NMR spectrum. However, on the basis of the similarity of the IR and ^{1}H NMR spectra of **6** to the rest of the compounds in the series, the most reasonable conclusion is that its structure is analogous and the ^{13}C NMR resonances are coincidental.

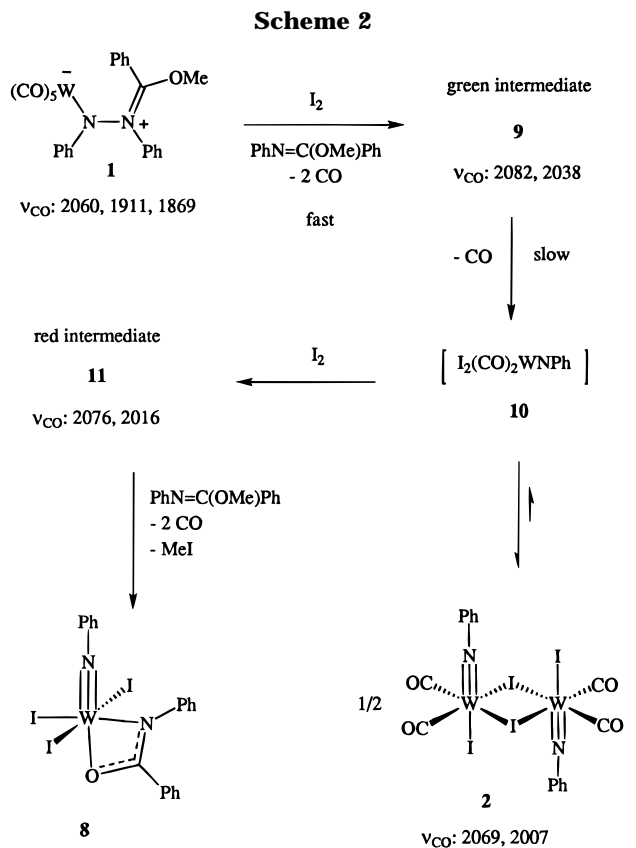(11) Massey, S. T. Ph.D. Dissertation, Stanford University, 1995.
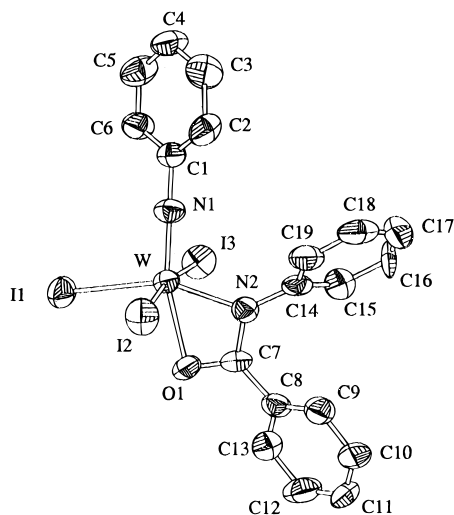
Figure 1. Thermal ellipsoid drawing of compound **8**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

crystals are obtained. An IR spectrum of the blue material revealed that all of the metal carbonyls had been lost from the starting material. ^{1}H and ^{13}C NMR spectra indicated three inequivalent phenyl groups, and the ^{13}C NMR resonance of the old imidate carbon could be found at 181.7 ppm. In addition, ^{1}H NMR spectra of reaction mixtures demonstrated clean conversion of zwitterion **1** to the blue product, and methyl iodide was detected as the only side product. Since the lack of carbonyl groups and additional protons other than phenyl made spectroscopic characterization difficult, the structure of **8** was determined by X-ray crystallography (eq 2).
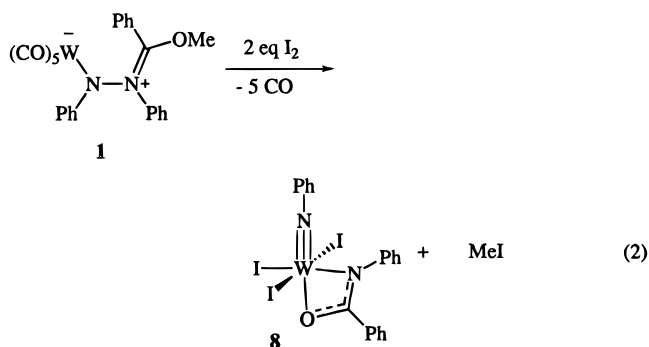
A thermal ellipsoid diagram of **8** is shown in Figure 1. The W center has a pseudooctahedral conformation, but it is heavily distorted due to the four-membered W−O1−C7−N2 ring with its O1−W−N2 bond angle of 60.1(5)°. The three terminal iodide ligands have an average bond length of 2.706 Å. As also seen in **2**, the short W−N1 bond length of 1.743(12) Å and nearly linear W−N1−C1 angle of 174.2(9)° are indicative of a W−N triple bond.[12] Other features of interest are the long W−N2 and W−O1 bond lengths of 2.063(14) and 2.238(11) Å, respectively.[13] The O1−C7 bond length of 1.26(2) Å is intermediate between the values for a single and double C_{sp^2}-O bond, indicating some double-bond character, while the C7−N2 bond of 1.36(2) Å is in the range of a C_{sp^2}-N single bond.[14] Complex **8** shares many

Scheme 2

structural similarities with the recently reported Mo bis-(carbamate) complex Mo(N-2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$[NPhC(O)O^t-Bu]$_2$,[15] which contains two Mo−N−C−O rings. The O−Mo−N angles of 59.59(7) and 58.63(7)° are very similar to the O1−W−N2 value of 60.1(5)° observed for **8**. The Mo−N and Mo−O bond lengths of 2.103(2) and 2.381(2) Å, respectively, are again close to the analogous values for **8**.

Mechanism for the Formation of Dimer 2 and Metallacycle 8. The proposed mechanism for the formation of dimer **2** and metallacycle **8** is shown in Scheme 2. Addition of 1 or 2 equiv of I$_2$ to a methylene chloride solution of zwitterion **1** results in immediate effervescence, and the solution turns green. An IR spectrum taken after 1 min in each reaction reveals that all of the zwitterion **1** (ν_{CO} 2060, 1911, 1869 cm^{-1}) has been consumed and the imidate PhN=C(OMe)Ph ($\nu_{C=N}$ = 1662 cm^{-1}) has been produced. The same two carbonyl stretches at 2082 and 2038 cm^{-1} are observed in the IR spectrum of each reaction mixture at this time, implying the same initial pathway and a common intermediate. The green intermediate (**9**) was assigned as I$_2$(CO)$_3$W≡NPh, since the presence of two carbonyl signals with high stretching frequencies in the IR spectrum is consistent with a (CO)$_3$W moiety[16] with very limited back-bonding to the carbonyl ligands. This green intermediate slowly disappears over time with effervescence. When only 1 equiv of I$_2$ is reacted with **1**, the carbonyl signals of dimer **2** grow in at the expense

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(13) The average bond lengths for W−NR$_2$ and W−OR are 1.952 and 1.900 Å, respectively: Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1−S83.

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of the green intermediate. This is consistent with loss of a labile carbonyl ligand from $I_2(CO)_3W\equiv NPh$ to give **10**, which quickly dimerizes. Note that effervescence observed during the conversion of the green intermediate **9** to dimer **2** implies that **9** has more than two CO ligands. This allows assignment of **9** as a $(CO)_3W$ species instead of a *cis*-$(CO)_2W$ species, which would also exhibit two strong CO stretches in the IR.

If excess I_2 remains in solution after formation of the green intermediate **9**, no dimer **2** is observed during the course of the reaction. Instead, further oxidation occurs and PhN=C(OMe)Ph is consumed to give metallacycle **8**. Additional information is provided by a control experiment where dimer **2**, which is presumably in equilibrium with a small amount of the unsaturated mononuclear complex **10**, is reacted with 1 equiv of I_2. Addition of I_2 to dimer **2** results in a cherry red solution after 20 min. An IR spectrum demonstrates that dimer **2** has been replaced by a new organometallic species (**11**) with carbonyl stretching frequencies at 2076 and 2016 cm^{-1}. Over the course of 2 h, this species decomposes to give an intractable material. However, introduction of PhN=C(OMe)Ph to the solutions of the red intermediate **11** resulted in a blue solution after 20 min. An IR spectrum confirmed that most of the imidate and all of the intermediate had been consumed, and ^1H NMR spectroscopy showed the presence of metallacycle **8** and MeI. Therefore, we propose that attack of I_2 on **10** produces $[I_3(CO)_2W\equiv NPh]^+$ or a similar electron-poor species as the transient red intermediate **11**.[17] Any such d^0 species would have extremely labile carbonyl ligands and should also be prone to nucleophilic attack by the imidate (which is a poor nucleophile). Note that during formation of the metallacycle the original imidate methyl group is lost. The observation of MeI in the reaction mixtures is consistent with its removal via nucleophilic attack by I^-.

The postulated intermediates $I_2(CO)_3W\equiv NPh$ and $[I_3(CO)_2W\equiv NPh]^+$ are highly unusual species and bear some comment. $I_2(CO)_3W\equiv NPh$ is a d^2 complex with three competing π-acids, and $[I_3(CO)_2W\equiv NPh]^+$ is a d^0 species with two π-acids. Thus, back-donation to the metal carbonyls is expected to be extremely weak or, in the case of $[I_3(CO)_2W\equiv NPh]^+$, nonexistent. The limited π-back-donation in the green intermediate **9** and the red intermediate **11** is evidenced by the high carbonyl stretching frequencies in the IR spectrum of each, yet clearly some donation is occurring since the frequencies are much lower than that of free CO (ν_{CO} 2143 cm^{-1}). In carbonyl adducts where back-donation is not possible, the carbonyl stretching frequencies are found to be higher than that of free CO.[18] However, the formal oxidation state of the metal center is not an adequate indicator of its back-bonding capability. Other ligands on the metal may be involved in metal–carbonyl bond-

ing by providing the required electron density. This type of interaction has been proposed for d^0 zirconocene carbonyl species, where the carbonyl stretching frequency is lowered through the interaction of the π^* CO orbital with orbitals primarily associated with M–L bonding to the ancillary ligands.[19] Moreover, structural and kinetic studies have provided convincing evidence for three-centered bonding between the imido ligand, the metal center, and the carbonyl π^* orbital in d^2 imido complexes.[3] In the case of $I_2(CO)_3W\equiv NPh$ and $[I_3-(CO)_2W\equiv NPh]^+$, the CO π^* orbitals could receive additional electron density from the iodide ligands. A strong precedent exists for direct donation of electron density from a halide p_σ orbital into the π^* orbitals of *cis*-carbonyl ligands, an effect which is particularly significant in iodides.[20] These types of interactions may become more pronounced in metal complexes with very few d electrons and multiple carbonyl ligands. With respect to the low carbonyl stretching frequencies observed in the IR spectra for intermediates **9** and **11** (compared to free CO), a combination of electron donation from the imido ligand and iodides could weaken the C–O π-bond to an extent that is unanticipated, given the formal oxidation state of the metal.

Experimental Section

General Considerations. Standard inert-atmosphere Schlenk, cannula, and glovebox techniques and freshly distilled solvents were used in all experiments unless stated otherwise. Diethyl ether and tetrahydrofuran were distilled from sodium/benzophenone. Toluene was distilled over sodium. Chloroform, methylene chloride, and hexane were distilled over calcium hydride. All NMR solvents were degassed by three freeze–pump–thaw cycles and then stored in an inert-atmosphere glovebox over 3 Å molecular sieves. All other chemicals were purchased in reagent grade and used with no further purification unless stated otherwise.

$(CO)_5W=C(OMe)Ph$ was prepared according to the method of Fischer.[21] *cis*-Azobenzene was prepared according to the method of Cook.[22] The imidate PhN=C(OMe)Ph was synthesized according to the method reported by Lander.[23]

^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 300 or a General Electric QE 300 spectrometer. IR spectra were recorded on a Perkin-Elmer 1600 FTIR. Elemental analysis and high-resolution mass spectrometry were performed by the University of Florida analytical service.

Synthesis of $(CO)_5WNPhNPhC(OMe)Ph$ (1). The following procedure is a modification of the previously published method.[9a] A solution of *cis*-azobenzene (2.00 g, 11.0 mmol) in 50 mL of hexane was added to a solution of $(CO)_5W=C(OMe)$-Ph (4.86 g, 11.0 mmol) in 50 mL of hexane. The solution immediately turned dark greenish black. After 5 min of stirring at room temperature an additional 100 mL of hexane was introduced and the reaction mixture cooled to −30 °C for 12 h. Zwitterion **1** precipitated out of solution as a fine black powder (4.73 g, 79% yield) which was collected by filtration and washed with 3 × 20 mL aliquots of cold hexane. ^1H NMR

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(CDCl$_3$): δ 7.62 (m, 2H), 7.55 (m, 3H), 7.46 (m, 3H), 7.38 (m, 2H), 6.99 (t, 2H), 6.61 (d, 2H), 6.46 (t, 1H), 3.81 (s, OMe, 3H). ^{13}C NMR (CDCl$_3$, −20 °C): δ 203.16 (*trans* CO), 198.46 (*cis* CO), 171.97 (C=N), 160.34, 139.47, 132.73, 130.64, 129.71, 128.71, 128.65, 126.32, 125.50, 125.44, 115.48, 114.73 (Ph), 61.78 (OMe). IR (CH$_2$Cl$_2$): ν_{WCO} 2060, 1911, 1869 cm^{-1}. Anal. Calcd for C$_{25}$H$_{18}$N$_2$O$_6$W: C, 47.95; H, 2.90; N, 4.47. Found: C, 48.19; H, 2.81; N, 4.38.

Synthesis of [(CO)$_2$W(NPh)I$_2$]$_2$ (2). A solution of I$_2$ (1.65 g, 6.05 mmol) in 15 mL of dry ether was quickly added via cannula to a freshly prepared solution of 4.00 g (6.39 mmol) of zwitterion **1** in 40 mL of ether. The reaction mixture immediately began to effervesce and turned green. After 10–15 min of stirring, the red dimer **2** began to precipitate. The reaction mixture was stirred for 2 h, and then dimer **2** was collected as a fine red powder by filtration and washed with 2 × 10 mL of ether (2.86 g, 76.5% yield). Spectral data for **2** prepared in this manner are identical with those obtained on samples prepared as originally reported.[8]

Synthesis of W(NPh)I$_2$(CO)$_2$(THF) (3). Dimer **2** (300 mg, 0.258 mmol) was dissolved in 5 mL of THF to give a green solution, which was stirred for 2 h. Removal of the solvent gave a green oil which was contaminated with some THF and **2**. Attempts to remove the free THF under vacuum led to increased amounts of **2**. IR (CH$_2$Cl$_2$): ν_{CO} 2066, 1988 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.70−7.20 (m, Ph), 4.73 (m, THF), 2.14 (dt, THF). ^{13}C NMR (CDCl$_3$): δ 212.7 (CO, J_{WC} = 173.6 Hz), 207.0 (CO, J_{WC} = 168.6 Hz), 153.2, 129.5, 129.2, 124.8 (Ph), 81.1, 26.6 (THF).

Synthesis of W(NPh)I$_2$(CO)$_2$(CH$_3$CN) (4). Dimer **2** (2.33 g, 2.00 mmol) was added to 105 mL of CH$_3$CN. The dimer is initially insoluble but eventually disappears after 30 min of stirring to give a dark green solution. The solution was stirred for an additional 8 h; then the solvent was removed under vacuum to give **4** as a pure solid in 93% yield (2.17 g). IR (CH$_2$Cl$_2$): ν_{CO} 2072, 2003 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.60−7.20 (m, 5H, Ph), 2.78 (s, 3H, Me). ^{13}C NMR (CDCl$_3$): δ 206.4, 203.0 (CO), 135.0, 129.9, 129.2, 125.0, 103.4, 4.6 (Me). HRMS (FAB): found 597.8228 (M$^+$ − CO), calcd 597.8234.

Synthesis of W(NPh)I$_2$(CO)$_2$(py) (5). To a stirred solution of **2** (0.939 g, 0.803 mmol) in CH$_2$Cl$_2$ (25 mL) was added 2 equiv of pyridine (0.13 mL, 1.6 mmol). After 20 min, the solution had changed from red to a red/green dichroic solution. After 2 h, the solution was reduced to about 10 mL and toluene (20 mL) was added. Upon addition of hexane to the solution, **5** precipitated as a green solid (0.746 g, 70% yield). IR (CH$_2$Cl$_2$): ν_{CO} 2068, 1992 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 9.40 (dd, 2H), 7.94 (tt, 2H), 7.51 (m, 3H), 7.27 (m, 3H). ^{13}C NMR (CDCl$_3$): 208.3, 207.6, 154.9, 153.1, 139.5, 129.5, 129.2, 125.7, 124.8. Anal. Calcd for C$_{13}$H$_{10}$I$_2$N$_2$O$_2$W: C, 23.52; H, 1.52; N, 4.22. Found: C, 23.80; H, 1.53; N, 4.21.

Synthesis of W(NPh)I$_2$(CO)$_2$(NEt$_3$) (6). Dimer **2** (2.52 g, 2.16 mmol) was dissolved in 30 mL of THF, and then 1.20 mL (8.61 mmol) of triethylamine was added and the mixture stirred overnight. Removal of the solvent and excess triethylamine gave a green oil, which became a solid under high vacuum (crude yield: 95%). The residue was taken up in 20 mL of CH$_2$Cl$_2$, and hexane (25 mL) was added to precipitate **6** as a red/black solid which was isolated by filtration in 70% yield (2.03 g). IR (CH$_2$Cl$_2$): ν_{CO} 2058, 1984 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.5−7.1 (5H, Ph), 3.38 (dq, 6H, CH$_2$), 1.39 (t, 9H, CH$_3$). ^{13}C NMR (CDCl$_3$): δ 208.3 (2 CO, coincident), 155.1, 129.2, 128.1, 124.1 (Ph), 65.8, 15.3 (Et). HRMS (FAB): found 657.9167 (M$^+$ − CO), calcd 657.9158.

Synthesis of W(NPh)I$_2$(CO)$_2$(2,3,5-Me$_3$C$_6$H$_2$NH$_2$) (7). To a stirred solution of dimer **2** (2.00 g, 1.72 mmol) was added 2 equiv of 2,4,6-trimethylaniline (0.51 mL, 3.4 mmol). After about 5 min, a color change from red to dark purple had occurred. The CH$_2$Cl$_2$ was then removed under vacuum, and the resulting dark red powder (1.42 g, 91% yield) was washed with 50 mL of hexane, followed by 25 mL of 1:1 ether/hexane. The resulting powder was isolated by filtration. IR (CH$_2$Cl$_2$):

ν_{CO} 2064, 1984 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.38 (t, 1H), 7.15 (t, 2H), 6.81 (m, 4H), 6.45 (d, 1H, NH), 5.62 (d, 1H, NH), 2.43 (s, 6H, *o*-Me), 2.27 (s, 3H, *p*-Me). ^{13}C NMR (CDCl$_3$): δ 209.1, 207.2 (CO), 139.3, 135.4, 129.2, 129.1, 129.0, 127.0, 124.8, 20.6, 19.0. Anal. Calcd for C$_{17}$H$_{18}$I$_2$N$_2$O$_2$W: C, 28.50; H, 2.50; N, 3.91. Found: C, 28.30; H, 2.44; N, 3.73.

Synthesis of I$_3$(PhN)WNPhCPhO (8). To a stirred solution of zwitterion **1** (1.00 g, 1.60 mmol) in 20 mL of CH$_2$Cl$_2$ was added 2 equiv of I$_2$ (0.81 g, 3.20 mmol) in 10 mL of CH$_2$Cl$_2$. Immediate effervescence was observed, and the solution became green. After approximately 20−30 min the solution had undergone a color change from dark green to dark blue. The solvent and methyl iodide were removed under vacuum, and a dark blue microcrystalline powder was obtained (1.29 g, 95% yield). X-ray-quality crystals were obtained by redissolving the blue powder in a minimum amount of CH$_2$Cl$_2$, cooling the solution to −40 °C for a period of 1 week, and isolating the crystals by filtration. ^{1}H NMR (CDCl$_3$): δ 7.65 (m, 5H), 7.30 (m, 5H), 7.12 (m, 2H), 6.98 (m, 3H). ^{13}C NMR (CDCl$_3$): δ 181.7, 149.8, 145.5, 134.4, 133.4, 130.5, 129.9, 129.4, 128.8, 128.0, 127.3, 121.9. Anal. Calcd for C$_{19}$H$_{15}$I$_3$N$_2$OW: C, 26.76; H, 1.76; N, 3.28. Found: C, 26.37; H, 1.55; N, 2.60.

Reaction of Zwitterion 1 with 1.25 Equiv of I$_2$. I$_2$ (25 mg, 0.10 mmol) was dissolved in 15 mL of CHCl$_3$ and added to 50 mg (0.080 mmol) of zwitterion **1**. Immediate effervescence was observed, and the reaction mixture turned green. An IR spectrum taken after 1 min showed that zwitterion **1** (ν_{CO} 2060, 1911, 1869 cm^{-1}) had been completely consumed and large amounts of imidate ($\nu_{C=N}$ = 1662 cm^{-1}) had been produced. Carbonyl signals at 2082 and 2038 cm^{-1} were observed at that time. IR spectra taken periodically over 3 h showed that the carbonyl stretching frequencies for dimer **2** grow in at the expense of the green intermediate (ν_{CO} 2082, 2038 cm^{-1}).

Reaction of Zwitterion 1 with 2.5 Equiv of I$_2$. I$_2$ (50 mg, 0.20 mmol) was dissolved in 20 mL of CHCl$_3$ and added to 50 mg (0.080 mmol) of zwitterion. Immediate effervescence was observed, and the reaction mixture turned green. An IR spectrum taken after 1 min showed that zwitterion **1** (ν_{CO} 2060, 1911, 1869 cm^{-1}) had been completely consumed and large amounts of imidate ($\nu_{C=N}$ = 1662 cm^{-1}) had been produced. Carbonyl signals at 2082 and 2038 cm^{-1} were observed at that time. After 10 min, the carbonyl and imidate signals had disappeared.

Reaction of Dimer 2 with I$_2$, Followed by Addition of PhN=C(OMe)Ph. Dimer **2** (100 mg, 0.086 mmol) was dissolved in 5 mL of CH$_2$Cl$_2$. I$_2$ (45 mg, 0.18 mmol) was added with stirring. Over 20 min, the solution became cherry red. An IR spectrum of the solution taken at that time revealed that dimer **2** had been completely consumed, and two new carbonyl signals at 2076 and 2016 cm^{-1} were present. Addition of 37 mg (0.18 mmol) of PhN=C(OMe)Ph resulted in a deep blue solution after 20 min. An IR spectrum taken at that time demonstrated that much of the imidate had been consumed. The solvent was removed, and ^{1}H NMR spectroscopy of the residue showed the presence of metallacycle **8** and methyl iodide.

Supporting Information Available: Tables of crystallographic data, bond distances, bond angles, positional parameters, and anisotropic displacement parameters for **8** (7 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.