Organometallics **1998,** *17,* 4037−4041

Oxidative Carbonylation of Primary Amines to Ureas Using Tungsten Carbonyl Catalysts[1]

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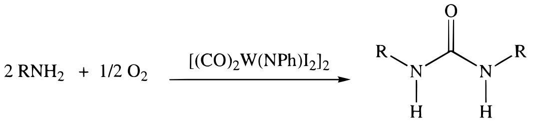
The iodo-bridged tungsten(IV) dimer $[(CO)_2W(NPh)I_2]_2$ (**1**) has been demonstrated to be a catalyst for the oxidative carbonylation of primary amines to 1,3-disubstituted ureas. The amine complexes $(CO)_2I_2W(NPh)(NH_2R)$ [R = *n*-Bu (**2a**), R = *n*-Pr (**2b**), R = *t*-Bu (**2c**)] and $[(CO)_2IW(NPh)(NH_2R)_2]^+$ [R = *n*-Bu (**4a**), R = *n*-Pr (**4b**)] have been isolated from reactions of **1** with primary amines. Complexes **2a**−**c** and **4a**−**b** have been shown to lie along the pathway to the catalytically active species. In addition, it has been determined that primary amines can be oxidatively carbonylated to 1,3-disubstituted ureas using $W(CO)_6$ as catalyst and I_2 as the oxidant.

Introduction

Although transition metal-catalyzed carbonylation reactions have been investigated extensively over many years,[2] the topic remains of interest. Oxidative conversion of primary amines into ureas[3] and the related conversion of primary amines into carbamates[4] have been the subject of multiple reports. Catalysts involving Ni,[3b] Co,[3d,4f] Rh,[4g,h] Mn,[3c,5,6] Ru,[3a,4g,h] and, most commonly, Pd[3e,4] have been demonstrated to carry out this reaction. However, although many transition metal systems have been examined, carbonylation reactions involving group 6 metals[7,8] still remain rare.

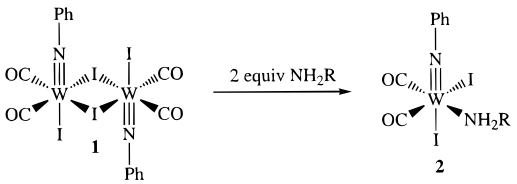
We recently reported the carbonylation of primary amines to ureas using the iodo-bridged dimer $[(CO)_2W(NPh)I_2]_2$ (**1**) as a stoichiometric reagent (eq 1).[9] We now report catalytic oxidative carbonylation of primary amines using **1** as the precatalyst. In addition, further mechanistic information on the process is provided. During the course of these studies, we also determined that primary amines could be carbonylated to 1,3-disubstituted ureas using $W(CO)_6$ as precatalyst and I_2 as the oxidizing agent.



(1)

Results and Discussion

Mechanistic Studies. To obtain mechanistic information about the carbonylation of amines by **1**, the necessary equivalents of amine were added in a stepwise manner. As shown in eq 2, reaction of **1** with 2 equiv of primary amine yielded the complexes $(CO)_2I_2W(NPh)(NH_2R)$ (**2**), in which the iodo-bridges of **1** have been replaced by amine ligands. Similar conversions of **1** to mononuclear complexes by addition of two-electron donor ligands have been described previously.[10] Primary amine complexes derived from *n*-butylamine (**2a**), *n*-propylamine (**2b**), and *tert*-butylamine (**2c**) were prepared, establishing that this is a general reaction. In addition, compounds **2a**, **2b**, and **2c** can also be generated by reacting the previously reported acetonitrile complex $(CO)_2I_2W(NPh)(NCCH_3)$ (**3**) with 1 equiv of amine (eq 3).[10]



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[1] Dedicated to Professor Warren Roper on the occasion of his 60th birthday.

[2] For monographs on the topic, see: (a) Colquhoun, H. M.; Thompson, D. J.; Twigg, M. V. *Carbonylation: Direct Synthesis of Carbonyl Compounds*; Plenum: New York, 1991. (b) Sheldon, R. A. *Chemicals from Synthesis Gas*; Dordrecht: Boston, 1983. (c) Wender, I.; Pino, P. *Organic Syntheses via Metal Carbonyls*; Wiley-Interscience: New York, 1968.

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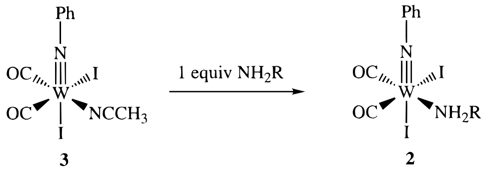
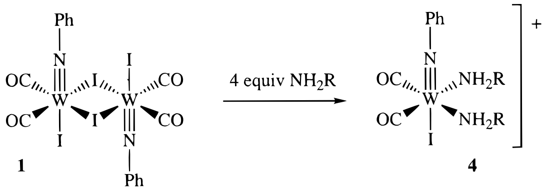


(3)

Amine complexes **2a**−**c** have been characterized by comparison of their spectral data to those of similar species.[9,10] The ^{1}H NMR spectra of **2a**−**c** reflect the chirality at the metal center. The diastereotopic NH$_2$ protons are seen as two broad singlets at 4.33 and 4.02 ppm for **2a** and 4.35 and 4.03 ppm for **2b,** while for **2c** they appear as two sets of doublets at 4.83 and 4.07 ppm. The ^{13}C spectra of these complexes all exhibit two inequivalent carbonyl signals, which allow assignment of the carbonyl ligands as cis. Additional evidence for the stereochemistry at the metal can be found in the two IR stretches for the cis-carbonyl ligands.

Reaction of **1** with 4 equiv of a primary amine produces the [(CO)$_2$IW(NPh)(NH$_2$R)$_2$]$^+$ complex **4** (eq 4), in which one of the iodide ligands of **2** has been replaced by an amine. The *n*-butylamine (**4a**) and *n*-propylamine derivatives (**4b**) have been successfully synthesized in this manner. These bis(amine) cations are also available via reaction of **2a,b** with 1 equiv of the corresponding amine or by addition of 2 equiv of amine to **3**. The ^{1}H NMR spectra of these complexes exhibit diastereotopic NH$_2$ protons at 5.4 and 4.7 ppm for **4a** and at 5.2 and 4.9 ppm for **4b**. The ^{13}C spectra of these complexes contain one carbonyl signal each, as well as only one set of alkyl signals. The stereochemical assignment of the carbonyl ligands as cis derives from the two IR stretches at 2060 and 1989 cm^{-1} for both **4a** and **4b**.

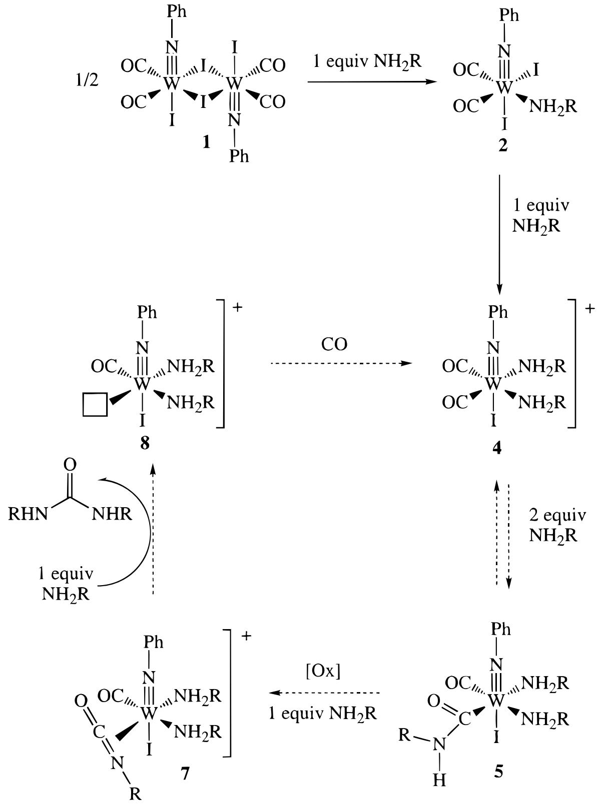


(4)

The monomeric amine complexes were demonstrated to be on the reaction pathway by reaction of amine complexes **2a**, **2b**, and **2c** with excess amine under oxidative conditions. As expected, the corresponding 1,3-disubstituted ureas were produced. Similar experiments involving the cationic bis(amine) complexes **4a** and **4b** established that the reaction pathway was also accessible from these species. Attempts to isolate complexes further along the pathway by reaction of **1** with additional equivalents of amine proved to be unsuccessful.

Although the remaining intermediates in the carbonylation process were too reactive to be characterized, literature precedent and the results of further experiments (vide infra) suggest the mechanism shown in Scheme 1. IR spectra of unoxidized reaction mixtures of **1** with *n*-butylamine exhibited a stretch at 1589 cm^{-1}, consistent with the presence of carbamoyl ligands.[11] Intermediacy of carbamoyl complex **5** (Scheme 1) or a related species is supported by Angelici's work on the carbonylation of CH$_3$NH$_2$ by [(η^5-C$_5$H$_5$)W(CO)$_4$]PF$_6$,[7] for which the first step is conversion of [(η^5-C$_5$H$_5$)W(CO)$_4$]$^+$ to the carbamoyl complex (η^5-C$_5$H$_5$)W(CO)$_3$(CONHCH$_3$) upon reaction with 2 equiv of CH$_3$NH$_2$. Formation of **5** from **4** would require an analogous nucleophilic attack of the amine on a carbonyl ligand, followed by deprotonation with a second equivalent of the amine. The carbonyl stretching frequency of 2066 cm^{-1} for **4** falls within the range where nucleophilic attack is expected to occur,[11a] rendering the conversion of **4** to **5** a reasonable possibility.

Scheme 1



Given that the carbamoyl IR stretches disappear upon exposure of the reaction mixtures to air, the next step in the mechanism appears to be oxidation. Upon oxidation of the complex, the carbamoyl proton would become more acidic. Deprotonation of **5** by the excess amine would form an isocyanate complex such as **7**. Although isocyanates are likely intermediates in the carbonylation of amines by **1** and have been isolated from the reaction of Et$_3$N with (η^5-C$_5$H$_5$)W(CO)$_3$-(CONHCH$_3$),[7] no free or coordinated isocyanates have been detected in the reaction mixtures of amines with **1**. However, nucleophilic attack of an amine on either cationic isocyanate complex **7** or the free isocyanate to form the 1,3-disubstituted ureas would be expected to be facile.

A less well-precedented mechanistic option is deprotonation of one of the amine ligands of **4**, followed by migratory insertion of the carbonyl into the tungsten−nitrogen bond. A similar sequence has been reported by Wang for a dicarbonyl rhenium cation bearing an amine tethered to a Cp ring.[12] In this system, depro-

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(11) (a) Angelici, R. J. *Acc. Chem. Res.* **1972**, *5*, 335−341. (b) Anderson, S.; Cook, D. J.; Hill, A. F. *Organometallics* **1997**, *16*, 5595−5597.

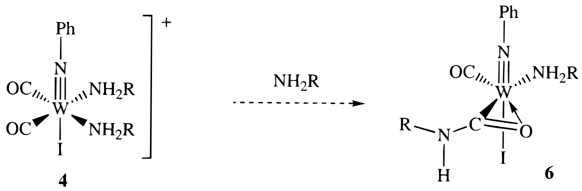
(12) Wang, T.-F.; Hwu, C.-C.; Tsai, C.-W.; Wen, Y.-S. *Organometallics* **1998**, *17*, 131−138.

Table 1. Catalytic Carbonylation of *n*-Butylamine Using Dimer 1

catalyst	oxidant	TON[a]
1	I_2	15[b]
1	I_2	25[c]
1	PhIO	12[b]
1	Me_3NO	0.4[b]
1	*t*-BuOOH	1.2[b]
1	*t*-BuOO-*t*-Bu	1.2[b]
1	Ce(IV)	6[b]
1	$CuCl_2$	4[b]
1	air	1.2[d]

[a] Turnover number per equivalent of dimer **1**. [b] Reaction conditions: amine (22 mmol), oxidizing agent (22 mmol), CO (100 atm), dimer **1** (0.22 mmol), room temperature, 24 h. [c] Reaction conditions: amine (22 mmol), oxidizing agent (22 mmol), CO (100 atm), K_2CO_3 (22 mol), dimer **1** (0.22 mmol), room temperature, 24 h. [d] Reaction conditions: amine (71 mmol), CO (800 psi), air (200 psi), dimer **1** (0.24 mmol), room temperature, 24 h.

tonation of the coordinated amine triggers CO insertion to produce an η^2-carbamoyl complex. Further addition of a two-electron donor ligand converts the carbamoyl to an η^1 configuration. Application of this sequence to amine complex **4** would produce η^2-carbamoyl complex **6** (eq 5). Addition of another equivalent of amine to **6** would produce intermediate **5**, at which point this route would converge with Scheme 1.[13]



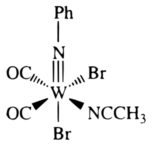
4 **6** (5)

Catalytic Carbonylation of Amines to Ureas. The mechanism proposed in Scheme 1 raised the interesting possibility that the reaction could be rendered catalytic in the presence of excess CO. As shown in Scheme 1, loss of isocyanate from **7** would yield the unsaturated intermediate **8**. Addition of CO to **8** would regenerate bis(amine) complex **4**, closing the catalytic cycle.

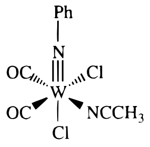
The expectation that the catalytic cycle could be closed was confirmed by providing excess CO to the reaction mixture. For example, when **1**, 100 equiv of *n*-butylamine, and 100 equiv of the oxidizing agent iodosylbenzene were placed in a 125 mL Parr high-pressure vessel and pressurized with 100 atm CO, di-*n*-butylurea was produced in an amount corresponding to 12 turnovers per equivalent of dimer **1** (Table 1).[14]

Before catalytic reactions were studied further, effort was devoted to optimizing conditions for the stoichiometric reaction. Use of chlorinated solvents (CH_2Cl_2, $CHCl_3$, or CCl_4) resulted in the highest yields of product. Ureas were also formed in coordinating solvents such as acetonitrile and THF. However the yields were quite low, probably because these solvents compete with the amines for coordination sites. Since the starting dimer **1** is insoluble in most other common solvents, the range of usable solvents is limited.

The use of iodide complexes or the addition of iodine-containing promoters[3e,4b,d,f−i] is common in the literature on oxidative carbonylation, especially in Pd-catalyzed reactions. Since the role of the iodide ligands in the reactivity of **1** was unclear, a comparison of different halide ligands was carried out using complexes **3**, **9a**, and **9b**.[15] When iodide complex **3** was reacted with 10 equiv of *n*-butylamine under the stoichiometric conditions, 0.5 equiv of di-*n*-butylurea was produced per equivalent of **1**. In similar experiments, the bromide complex **9a** and the chloride complex **9b** were reacted with excess primary amines under the stoichiometric oxidative conditions. However, neither **9a** nor **9b** successfully formed ureas or any other detectable organic products, thus indicating that iodide ligands are necessary for the carbonylation reaction.



9a



9b

In efforts to determine the optimum conditions for catalytic conversion of primary amines to ureas, several oxidizing agents were examined (Table 1). Since iodide ligands facilitate the carbonylation reaction, I_2 was a reasonable choice as an oxidizing agent.[3e,4b,16] In fact, I_2 was the most effective oxidant examined, as measured by the number of catalyst turnovers. The addition of K_2CO_3 also proved to be important.[3e,4b,16] In the absence of added base, the turnovers are limited by the production of 2 equiv of the amine hydroiodide (RNH_3I) per equivalent of urea. If the reaction is run in the presence of K_2CO_3, the amine salt byproduct can be recycled. Upon addition of K_2CO_3 to the I_2-oxidized reaction, di-*n*-butylurea was produced in an amount corresponding to 25 turnovers per equivalent of dimer **1**, or 52% yield with respect to amine (Table 1).

Among the other oxidants that were examined, iodosylbenzene gave the best results of the oxo transfer reagents. Other oxo transfer reagents such as trimethylamine *N*-oxide also work but tend to be problematic when not extremely dry, since the carbonylation reaction is moisture sensitive. In the presence of water, yields of ureas are low. For this reason, hydrogen peroxide is a poor choice as oxidizing agent. Di-*tert*-butylperoxide and *tert*-butylhydroperoxide do induce carbonylation of amines by **1**, although multiple turnovers cannot be obtained and several unidentified side products are also formed. Outer sphere oxidants, such as Ce(IV) and $CuCl_2$, rendered the reaction catalytic as well. Since the original stoichiometric conditions uti-

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(13) A reviewer has suggested a third mechanistic option in which oxidation of **5** leads to the preferential deprotonation of an amine ligand instead of the carbamoyl ligand. Reductive elimination from the resulting carbamoyl-amido complex $[(CO)IW(NPh)(NH_2R)(NHR)(CONHR)]^+$ would then yield the urea. We cannot rule out this alternative. However, we still favor the mechanism shown in Scheme 1 due to the literature precedent in ref 6 and our observation of small amounts of isocyanates in some of the reaction mixtures by GC. The GC evidence should be viewed with some skepticism since the observed isocyanates could arise from cracking of labile species in the injection port. However, their presence does provide some support for Scheme 1.

(14) Note that since dimer **1** is cleaved to mononuclear complexes in the presence of amines, each tungsten is turning over six times. However, since the tungsten was added to the reaction mixtures in the form of **1**, the yields are reported on this basis.

(15) He, Y.-X., McGowan, P. C.; Abboud, K. A.; McElwee-White, L. *J. Chem. Soc., Dalton Trans.*, in press.

(16) Dahlen, G. M.; Sen, A. *Macromolecules* **1993**, *26*, 1784−1786.

Table 2. Catalytic Carbonylation of *n*-Butylamine Using $W(CO)_6$

catalyst	equiv n-$BuNH_2$	equiv I_2	equiv K_2CO_3	time (h)	TON[a,b]
$W(CO)_6$	50			24	0
$W(CO)_6$	50	25		0.5	3
$W(CO)_6$	50	25		3	9
$W(CO)_6$	50	25		24	9
$W(CO)_6$	50	25	50	24	15
$W(CO)_6$	100	50	100	24	39

[a] Turnover number per equivalent of $W(CO)_6$. [b] Reaction conditions: CO (100 atm), $W(CO)_6$ (0.21 mmol), room temperature.

lized air as the oxidant, efforts were made to explore O_2 as the oxidant in the catalytic reaction. However, using a mixture of 800 psi CO and 200 psi air did not induce multiple catalyst turnovers, presumably because an intermediate species in the catalytic cycle is oxygen sensitive. For example, if the unsaturated complex **8** were to react with oxygen, the stoichiometric reaction would run in the presence of air as observed, but loss of **8** would prevent the reaction from turning over in the presence of O_2.

Catalytic Carbonylation of Amines with $W(CO)_6$ as Catalyst. Catalysis of amine carbonylation by **1** in the presence of iodine suggested that other tungsten carbonyl iodide complexes might also serve as catalysts. The simplest choice as precatalyst was the readily available, inexpensive, and air stable $W(CO)_6$. Control experiments for the catalytic carbonylation of *n*-butylamine were carried out using $W(CO)_6$ as catalyst, but omitting the I_2 oxidant. As expected, when $W(CO)_6$ and 50 equiv of *n*-butylamine are placed in a 125 mL Parr high-pressure vessel and pressurized with 100 atm CO, no di-*n*-butylurea is produced (Table 2). This is consistent with the conventional wisdom that group 6 metal complexes are poor carbonylation catalysts.[8]

However, when $W(CO)_6$, 50 equiv of *n*-butylamine, and 25 equiv of iodine are placed in a 125 mL Parr high-pressure vessel and pressurized with 100 atm CO, di-*n*-butylurea is produced in an amount corresponding to 9 turnovers per equivalent of $W(CO)_6$ (Table 2). As discussed in conjunction with experiments involving dimer **1** (vide supra), oxidative carbonylation of amines to ureas produces 2 equiv of amine hydroiodide per equivalent of urea. Once again, addition of K_2CO_3 to release the free amine from the salt increases the turnover number dramatically. Reaction of $W(CO)_6$, 100 equiv of *n*-butylamine, 50 equiv of iodine, and 100 equiv of K_2CO_3 in a 125 mL Parr high-pressure vessel pressurized with 100 atm CO produces di-*n*-butylurea in an amount corresponding to 39 turnovers per equivalent of $W(CO)_6$, or 80% yield with respect to amine (Table 2).

Additional control experiments included addition of I_2 in only a trace amount. Since the reaction was starved for oxidant, only a trace amount of urea was formed. The potential participation of the stainless steel walls of the reactor was probed by control experiments using a glass liner. The number of turnovers obtained in the presence and absence of the glass liner did not differ significantly with either $W(CO)_6$ or dimer **1** as the catalyst. Furthermore, the control experiment in which no catalyst was added but the solution was allowed to contact the stainless steel walls was also performed. A negligible amount of urea was detected, but the amount was not significant with respect to the quantities of urea obtained in the presence of the catalysts.

No mechanistic studies were performed on the $W(CO)_6$ system, but it is known that oxidation of $W(CO)_6$ with I_2 results in the formation of iodocarbonyl complexes that readily undergo ligand exchange with nucleophiles.[17,18] The mechanism is thus likely to follow a cycle similar to that proposed in Scheme 1 for the chemistry of dimer **1**.

Summary. We have developed mild methods to convert primary amines to 1,3-disubstituted ureas using dimer **1** as precatalyst and I_2 as the oxidant. A possible pathway involving carbamoyl and isocyanate complexes has been proposed. Based on the reactions of **1**, it was established that $W(CO)_6$ could also be used as a carbonylation catalyst in the presence of I_2 as the oxidant. These reactions are rare examples of catalytic carbonylation using a group 6 metal. Further work on related carbonylation reactions is in progress.

Experimental Section

General. Standard inert atmosphere Schlenk, cannula, and glovebox techniques and freshly distilled solvents were used in all experiments unless stated otherwise. Diethyl ether was distilled from sodium/benzophenone. Methylene chloride and hexane were distilled over calcium hydride. All NMR solvents were degassed by three freeze−pump−thaw cycles, 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. Authentic samples of the ureas were prepared from the corresponding amines and isocyanates.[19]

^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 300 spectrometer. IR spectra were recorded on a Perkin-Elmer 1600 FTIR. GC was performed on an HP5890 chromatograph containing a 30 m × 0.75 mm column of SPB-20 on fused silica. High-resolution mass spectrometry was performed by the University of Florida analytical service. Elemental analysis was performed by Robertson Microlit Laboratories.

Synthesis of $(CO)_2I_2W(NPh)(H_2NCH_2CH_2CH_2CH_3)$ (2a). To a stirred solution of dimer **1** (77 mg, 0.066 mmol) in 20 mL of CH_2Cl_2 was added 2 equiv of *n*-butylamine (0.013 mL, 0.13 mmol). A color change from red to purple occurred immediately. After 1 h of stirring the CH_2Cl_2 was removed under vacuum. The red oil was redissolved in 2 mL of CH_2Cl_2, and 5 mL of hexane was layered on top. The solution was placed in a −40 °C freezer overnight. The red solution was cannulated away from any precipitate and concentrated. The resulting red oil was collected into 50 mL of ether and cannulated away from any insoluble particles. The solvent was removed under vacuum to yield **2a** as a red oil (11 mg, 13% yield). IR (CH_2Cl_2): ν_{CO} 2066, 1988 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.50−7.21 (m, 5H), 4.33 (s, 1H), 4.02 (s, 1H), 3.37 (m, 2H), 1.68 (m, 2H), 1.44 (m, 2H), 0.98 (t, 3H). ^{13}C NMR ($CDCl_3$): δ 208.6, 208.5, 153.3, 129.5, 129.1, 124.9, 51.9, 34.6, 19.5, 13.4. HRMS (FAB): 629.886 $(M - CO)^+$; calcd, 629.8824. Lability of the compound precluded obtaining an elemental analysis.

Synthesis of $(CO)_2I_2W(NPh)(H_2NCH_2CH_2CH_3)$ (2b). To a stirred solution of dimer **1** (53 mg, 0.045 mmol) in 20 mL of

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(17) (a) Colton, R.; Rix, C. J. *Aust. J. Chem.* **1969**, *22*, 305−310. (b) Schmid, G.; Boese, R.; Welz, E. *Chem. Ber.* **1975**, *108*, 260−264. (c) Umland, P.; Vahrenkamp, H. *Chem. Ber.* **1982**, *115*, 3565−3579. (d) Schmid, G.; Boese, R. *Chem. Ber.* **1976**, *109*, 2148−2153.

(18) The reported reactions of I_2 with $W(CO)_6$ involve photolysis. However, the more complex carbonylation reaction mixtures may provide alternative pathways for oxidation.

(19) For a review on synthesis of ureas, see: Vishnyokova, T. P.; Golubeva, I. A.; Glebova, E. V. *Russ. Chem. Rev.* **1985**, *54*, 249−261.

CH_2Cl_2 was added 2 equiv of *n*-propylamine (0.0075 mL, 0.091 mmol). A color change from red to purple occurred immediately. After 1 h of stirring the CH_2Cl_2 was removed under vacuum. The red oil was redissolved in 2 mL of CH_2Cl_2, and 5 mL of hexane was layered on top. The solution was placed in a −40 °C freezer overnight. The red solution was cannulated away from any precipitate and concentrated. The resulting red oil was taken up into 50 mL of ether and cannulated away from any insoluble particles. The solvent was removed under vacuum to yield **2b** as a red oil (53 mg, 63% yield). IR (CH_2Cl_2): ν_{CO} 2067, 1988 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.50−7.26 (m, 5H), 4.35 (s, 1H), 4.03 (s, 1H), 3.34 (m, 2H), 1.75 (m, 2H), 1.04 (t, 3H). ^{13}C NMR ($CDCl_3$): δ 208.5, 208.4, 153.8, 129.4, 129.1, 124.9, 53.8, 25.8, 10.6. Lability of the compound precluded obtaining an elemental analysis.

Synthesis of $(CO)_2I_2W(NPh)(H_2NC(CH_3)_3)$ (2c). To a stirred solution of dimer **1** (113 mg, 0.097 mmol) in 20 mL of CH_2Cl_2 was added 2 equiv of *tert*-butylamine (0.020 mL, 0.195 mmol). A color change from red to purple occurred immediately. After 2 h of stirring the CH_2Cl_2 was removed under vacuum. The purple oil was redissolved in 2 mL of CH_2Cl_2, and 5 mL of hexane was layered on top. The solution was placed in a −40 °C freezer overnight. The red solution was cannulated away from any precipitate and concentrated. The resulting red solid was taken up into 50 mL of hexane and cannulated away from any insoluble particles. The solvent was removed under vacuum to yield **2c** as a red solid (45 mg, 70% yield). IR (CH_2Cl_2): ν_{CO} 2067, 1987 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.49−7.18 (m, 5H), 4.83 (d, 1H), 4.07 (d, 1H), 1.44 (t, 9H). ^{13}C NMR ($CDCl_3$): δ 210.3, 207.5, 153.3, 129.5, 129.2, 124.9, 55.8, 30.8. HRMS (FAB): 629.886 $(M - CO)^+$; calcd, 629.8824. Lability of the compound precluded obtaining an elemental analysis.

Synthesis of $[(CO)_2IW(NPh)(H_2NCH_2CH_2CH_2CH_3)_2]I$ (4a). To a stirred solution of dimer **1** (100 mg, 0.086 mmol) in 20 mL of CH_2Cl_2 was added 4 equiv of *n*-butylamine (0.034 mL, 0.344 mmol) at 0 °C. A color change from red to maroon occurred immediately. After 2 h of stirring, the CH_2Cl_2 was removed under vacuum. The red oil was redissolved in 2 mL of CH_2Cl_2, and 25 mL of ether was added. The solution was placed in a −40 °C freezer for 2 days. The resulting orange powder (**4a**) was isolated by filtration (43 mg, 40% yield). IR (CH_2Cl_2): ν_{CO}, 2060, 1989 cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.28 (m, 3H), 7.04 (d, 2H), 5.35 (s, 2H), 4.88 (s, 2H), 3.15 (m, 4H), 1.85 (m, 4H), 1.41 (m, 4H), 0.91 (t, 6H). ^{13}C NMR (CD_2Cl_2): δ 214.7, 154.5, 129.3, 127.5, 127.3, 50.1, 34.3, 20.5, 13.8. Lability of the compound precluded obtaining an elemental analysis.

Synthesis of $[(CO)_2IW(NPh)(H_2NCH_2CH_2CH_3)_2]I$ (4b). To a stirred solution of dimer **1** (111 mg, 0.094 mmol) in 25 mL of CH_2Cl_2 was added 8 equiv of *n*-propylamine (0.062 mL, 0.752 mmol) at 0 °C. A color change from red to maroon occurred immediately. After 1 h of stirring, the CH_2Cl_2 was removed under vacuum. The red oil was redissolved in 2 mL of CH_2Cl_2, and 25 mL of ether was added. The solution was placed in a −40 °C freezer for 2 days. The resulting orange powder (**4b**) was isolated by filtration (30 mg, 26% yield). IR (CH_2Cl_2): ν_{CO}, 2060, 1989 cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.29 (m, 3H), 7.06 (d, 2H), 5.32 (s, 2H), 4.88 (s, 2H), 3.08 (m, 4H), 1.92 (m, 4H), 0.98 (t, 6H). ^{13}C NMR (CD_2Cl_2): δ 214.7, 154.5, 129.3, 127.5, 127.4, 52.1, 25.8, 11.6. Lability of the compound precluded obtaining an elemental analysis.

Catalytic Carbonylation of Primary Amines with 1 (Solid Oxidants). The following procedure is typical: To a stirred solution of dimer **1** (260 mg, 0.22 mmol) in 30 mL of CH_2Cl_2 was added 100 equiv of *n*-butylamine (2.2 mL, 22 mmol). A color change from red to deep purple occurred immediately. The solution was stirred under N_2 for 20 min, then added to a Parr high-pressure vessel, followed by addition of iodosylbenzene (4.9 g, 22 mmol). The vessel was then charged with 100 atm of CO and left to stir under pressure for 24 h. The pressure was released and the lemon yellow solution was then filtered through Celite and concentrated. The resulting yellow solid was dissolved in ethyl acetate and chromatographed on silica with ethyl acetate as eluent to obtain a white solid (616 mg, 3.59 mmol, 12 turnovers per equivalent of dimer **1**). The solid was identified as di-*n*-butylurea by comparison with an authentic sample.

Catalytic Carbonylation of Primary Amines with 1 (Air Oxidant). *Caution! High pressure mixtures of CO and O_2 are explosive under certain conditions.*[20] To a stirred solution of dimer **1** (278 mg, 0.24 mmol) in 50 mL of CH_2Cl_2 was added 300 equiv of *n*-butylamine (7.34 mL, 71 mmol). A color change from red to deep purple occurred immediately. The solution was stirred under N_2 for 20 min, then added to a Parr high-pressure vessel. The vessel was then charged with 800 psi of CO, followed by 200 psi of air, and left to stir under pressure for 24 h. The pressure was released, and the pale yellow solution was then filtered through Celite and concentrated. The resulting yellow oil was dissolved in ethyl acetate and chromatographed on silica with ethyl acetate as eluent to obtain a white solid (49 mg, 0.28 mmol, 1.2 turnovers per equivalent of dimer **1**). The solid was identified as di-*n*-butylurea by comparison with an authentic sample.

Catalytic Carbonylation of Primary Amines with $W(CO)_6$. The following procedure is typical: To a stirred solution of $W(CO)_6$ (75 mg, 0.21 mmol) in 25 mL of CH_2Cl_2 in the glass liner of a Parr high-pressure vessel was added 100 equiv of *n*-butylamine (2 mL, 21 mmol), K_2CO_3 (3.52 g, 21 mmol), and 50 equiv of iodine (2.56 g, 10.5 mmol). The vessel was then charged with 100 atm of CO and left to stir under pressure for 24 h. The pressure was released, and the maroon solution was filtered and then rinsed with a Na_2SO_3 solution. The resulting pale yellow solution was then dried with $MgSO_4$ and filtered. The solution was concentrated to yield a pale yellow solid, which was then rinsed with 25 mL of hexane. The solid was then taken up in 25 mL of ether and filtered to remove any residual $W(CO)_6$. The ether solution was concentrated to obtain a white solid (1.4 g, 8.13 mmol, 39 turnovers per equivalent of tungsten). The solid was identified as di-*n*-butylurea by comparison with an authentic sample.

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[20] Proper safety precautions against explosion hazards were employed during this work.