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Carbamoyl Complexes of Divalent Tungsten, Molybdenum, and Iron and the Unexpected Formation of an Aminomethylidyne Complex

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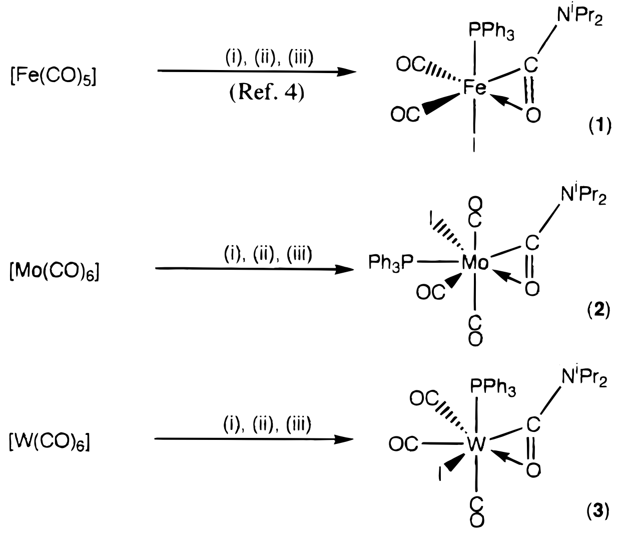
Summary: Sequential treatment of $[M(CO)_6]$ ($M = W$, Mo, but not Cr) with 1 equiv of LiN^iPr_2, iodine, and PPh_3 provides $[M(\eta^2\text{-}OCN^iPr_2)I(CO)_3(PPh_3)]$, which serve as precursors for a wide range of bidentate carbamoyl complexes; however, if for $M = W$, an excess of LiN^iPr_2 is employed, the aminomethylidyne complex $[W(\equiv CN^iPr_2)I(CO)_3(PPh_3)]$ is also obtained.

Carbamoyl (carboxamide) complexes of the group 6 metals have been prepared previously by a variety of routes.[1] Generally, these routes involve nucleophilic attack by amines on electrophilic carbonyl ligands, although notable examples of the C−H activation of formamides have also been observed.[2] As a class of ligands, carbamoyls have, however, been somewhat neglected, in favor of related acyl and aroyl ligands, for which a more direct industrial relevance to the catalytic activation of carbon monoxide is appreciated. Our studies on the synthesis of aminomethylidyne complexes[3] and in particular those of iron[4] have focused on the *O*-acetylation or phosphorylation of anionic carbamoylate complexes. Thus, e.g., the reaction of $[Fe\{=C(OLi)N^iPr_2\}(CO)_4]$ with $(CF_3CO)_2O$ and triphenylphosphine has been shown to be solvent dependent: In diethyl ether, the carbamoyl complex $[Fe(\eta^2\text{-}OCN^iPr_2)(CF_3)(CO)_2(PPh_3)]$ is obtained,[5] while in dichloromethane the aminomethylidyne salt $[Fe(\equiv CN^iPr_2)(CO)_3(PPh_3)](CF_3CO_2)$ is formed.[4] This aminomethylidyne complex has also been unexpectedly obtained from the reaction of $[Fe(\eta^2\text{-}OCN^iPr_2)(CF_3)(CO)_2(PPh_3)]$ with iodine,[4] and this unusual result has prompted us to investigate, in more detail, the oxidation of carbamoylate complexes. During studies on the iron system, a convenient entry point to carbamoyl complexes in general was found, based on the sequential treatment of $[Fe(CO)_5]$ with LiN^iPr_2, I_2 and PPh_3 to provide $[Fe(\eta^2\text{-}OCN^iPr_2)(CO)_2(PPh_3)]$ (**1**) (Scheme 1). Both this complex and its derivatives all displayed the less common bidentate η^2-O,C coordination mode for the carbamoyl ligand. We wished to establish whether this was a peculiarity for divalent iron or a more general feature of these ligands.

Scheme 1[a]



[a] Reagents and Conditions: Et_2O; (i) LiN^iPr_2, 25 °C; (ii) I_2, −78 °C; (iii) PPh_3, −78 to 25 °C.

Herein, we wish to report (i) the reactions of the carbamoylates $[M\{C(OLi)N^iPr_2\}(CO)_5]$ ($M = Mo$, W) with iodine, which provide convenient access to a wide range of carbamoyl complexes of these metals, the majority of which feature bidentate carbamoyl coordination. (ii) The reaction of $[W\{C(OLi)N^iPr_2\}_2(CO)_4]$ with iodine or bromine and triphenylphosphine, which unexpectedly provides the aminomethylidyne complexes $[W(\equiv CN^iPr_2)X(CO)_3(PPh_3)]$ ($X = Br$, I), via the presumed and unprecedented oxidative coupling of two carbamoyl ligands.

Treating $[M(CO)_6]$ ($M = Mo$, W) with LiN^iPr_2 provides the carbamoyl metalates $[M\{=C(OLi)N^iPr_2\}(CO)_5]$, which have previously served as entry points to the chemistry of aminomethyene and aminomethylidyne complexes of these metals.[6] Treating these compounds (generated in situ) with iodine results in the formation of thermolabile complexes presumed to be $[M(OCN^iPr_2)I(CO)_x]$ ($x = 4$, 5, ?); however, if triphenylphosphine is added subsequently, then stable derivatives $[M(\eta^2\text{-}OCN^iPr_2)I(CO)_3(PPh_3)]$ ($M = Mo$ (**2**), W (**3**)) are obtained in reasonable yields (40% (**2**), 45% (**3**)). The formulations follow from spectroscopic data[7] which confirm the gross composition but reveal an interesting difference in metal stereochemistry. In the case of **2**, a *fac*-$W(CO)_3$ geometry is adopted; however, for **3**, a *mer*-$Mo(CO)_3$ arrangement

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[1] (a) For a review of carbamoyl complexes; see: Angelici, R. J. *Acct. Chem. Res.* **1972**, *18,* 335. (b) For a more general review of η^2-acyl and related ligands, see: Durfee, L. D.; Rothwell, I. P. *Chem. Rev.* **1988**, *88,* 1059.

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[6] (a) Fischer, E. O.; Reitmeier, R.; Ackermann, K. *Z. Naturforsch., B.* 1984, *39,* 668 and references therein. (b) For a review covering the chemistry of aminomethylidyne complexes of these metals, see: Mayr, A.; Hoffmeister, H. *Adv. Organomet. Chem.* **1991**, *32,* 227.

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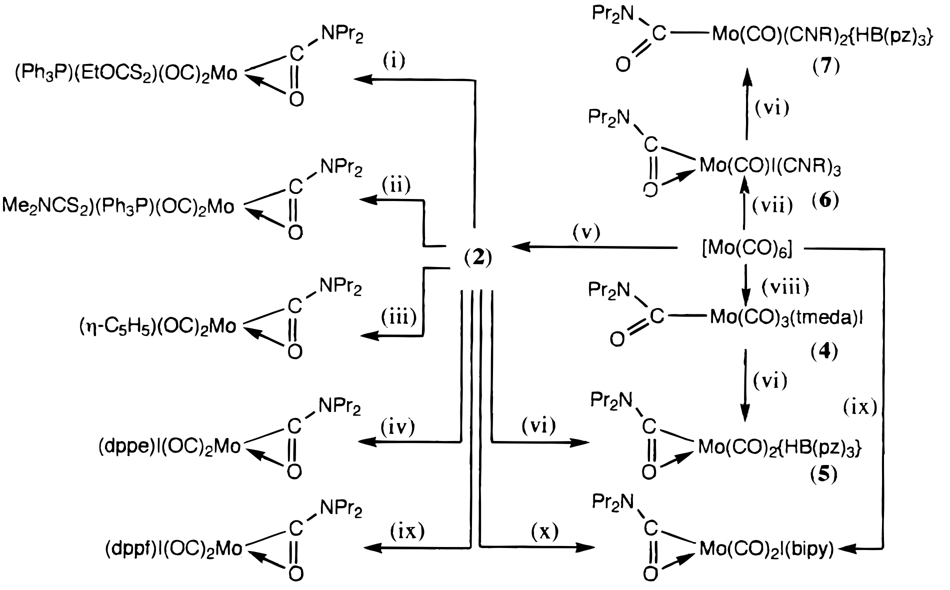
Scheme 2[a]



[a] Reagents: (i) K[EtOCS$_2$]; (ii) Na[S$_2$CNMe$_2$]; (iii) NaC$_5$H$_5$; (iv) dppe; (v) LiN^{i}Pr$_2$, I$_2$, PPh$_3$; (vi) K[HB(pz)$_3$]; (vii) LiN^{i}Pr$_2$, I$_2$, CNR (R = C$_6$H$_3$Me$_2$-2,6); (viii) LiN^{i}Pr$_2$, I$_2$, tmeda; (ix) dppf (1,1′-bis(diphenylphosphino)ferrocene); (x) bipy (2,2′-bipyridyl); (ix) LiN^{i}Pr$_2$, I$_2$, bipy.

results. The complexes **2** and **3** serve as stable and convenient precursors to a wide range of carbamoyl complexes via ligand exchange reactions: Scheme 2 illustrates the variety of carbamoyl complexes obtained so far for molybdenum. The tungsten analogue (**3**) has not yet been studied in detail but has so far provided the complexes [W(η^2-OCN^{i}Pr$_2$)(CO)$_2${HB(pz)$_3$}] (pz = pyrazol-1-yl) and [W(η^2-OCN^{i}Pr$_2$)I(CO)$_2$(dppe)] on treatment with K[HB(pz)$_3$] or dppe, respectively. While demonstrating the versatility of **2** and **3**, in developing the carbamoyl chemistry of these metals, the transformations are straightforward and call for little comment. One point which does, however, emerge from Scheme 2 is the prevalence of bidentate *(O,C)* carbamoyl coordination. Two complimentary sequences wherein this is not the case are noteworthy: Firstly, the complex [Mo{σ-C(=O)N^{i}Pr$_2$}I(CO)$_3$(tmeda)] (**4**) results from the reaction of **2** with tmeda or via a direct synthesis involving the sequential treatment of [Mo(CO)$_6$] with LiN^{i}Pr$_2$, I$_2$, and tmeda. On treating **4** with K[HB(pz)$_3$], the formation of [Mo(η^2-OCN^{i}Pr$_2$)(CO)$_2${HB(pz)$_3$}] (**5**) is accompanied by a conversion from *monohapto* to *dihapto* carbamoyl coordination. In contrast, the *dihapto* carbamoyl complex [Mo(η^2-OCN^{i}Pr$_2$)I(CO)(CNC$_6$H$_3$Me$_2$-2,6)$_3$] (**6**) (obtained from sequential treatment of [Mo(CO)$_6$] with LiN^{i}Pr$_2$, I$_2$, and CNC$_6$H$_3$Me$_2$-2,6) reacts with K[HB(pz)$_3$] to provide a *monohapto* carbamoyl complex [Mo{σ-C(=O)N^{i}Pr$_2$}(CO)(CNC$_6$H$_3$Me$_2$-2,6)$_2${HB(pz)$_3$}] (**7**). These observations, coupled with the temperature-dependent fluxionality evident in the ^{1}H NMR spectra of many of the complexes in Scheme 2, suggest to us that *monohapto–dihapto* interconversion is a low-energy process and may, in part, account for the facility of the ligand exchange reactions described.

Templeton has shown that the reaction of [Mo(η^2-OCMe)(CO)$_2${HB(pzMe$_2$-3,5)$_3$}] with excess sodium ethoxide results in the formation of the ethylidyne complex [Mo(≡CMe)(CO)$_2${HB(pzMe$_2$-3,5)$_3$}] in 20% yield.[9] A similar reaction ensues between [W(η^2-OCN^{i}Pr$_2$)(CO)$_2$-{HB(pz)$_3$}] and NaOEt, however, after heating in refluxing ethanol for 18 h, only approximately 10% conversion to [W(≡CN^{i}Pr$_2$)(CO)$_2${HB(pz)$_3$}] is observed. A more unusual carbamoyl/aminomethylidyne conversion occurs when [W(CO)$_6$] is treated with an excess (1.5–2 equiv) of LiN^{i}Pr$_2$ followed by I$_2$ and PPh$_3$. In addition to the anticipated carbamoyl complex **3**, the aminomethylidyne complex *mer*-[W(≡CN^{i}Pr$_2$)I(CO)$_3$-

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(7) Characteristic spectroscopic data for selected complexes (25 °C, IR (ν(CO), CH$_2$Cl$_2$), NMR (CDCl$_3$) satisfactory microanalytical, and FAB-MS data obtained): In a typical procedure the following method for the synthesis of **2** was followed: [Mo(CO)$_6$] (1.13 g) in diethyl ether (25 cm^3) was treated with LiN^{i}Pr$_2$ (2.9 cm^3, 1.5 mol dm^{-3}, Aldrich) and cooled (dry ice/propanone). Iodine (1.08 g) was added, the mixture allowed to warm to 0 °C, PPh$_3$ (2.34 g) added, and the mixture stirred for 10 h. The orange precipitate which formed was isolated and recrystallized from dichloromethane/hexane (−20 °C). Yield 1.20 g (40%, nonoptimized). IR(CH$_2$Cl$_2$): 2027, 1957, 1911 (ν(CO)), 1626 cm^{-1} (ν(NCO)). ^{1}H NMR (CDCl$_3$, 25 °C): 1.35, 1.38 (d × 2, 12 H, CH$_3$), 3.72, 4.35 (h × 2, 2 H, NCH), 7.21–7.60 (m, 15 H, C$_6$H$_5$) ppm. ^{13}C{^{1}H} NMR: 210.7, 209.8 (CO), 190.4 (NCO, J(PC) = 7 Hz), 133.9–130.2 (C$_6$H$_5$), 55.1, 50.1 (NCH), 20.9, 20.4 (CH$_3$) ppm. ^{31}P{^{1}H} NMR: 16.8 ppm. **1**: IR (CH$_2$Cl$_2$) 2021, 1953 (ν(CO)), 1610 cm^{-1} (ν(NCO)). ^{1}H NMR (CDCl$_3$, 25 °C): 0.55, 1.15, 1.19, 1.52 (d × 4, 12 H, CH$_3$), 3.35, 5.09 (h × 2, 2 H, NCH), 7.19–7.67 (m, 15 H, C$_6$H$_5$) ppm. ^{13}C{^{1}H} NMR: 220.5 (d, CO, J(PC) = 25.0 Hz), 212.4 (d, CO, J(PC) = 20.8 Hz), 197.4 (NCO, J(PC) = 19.4 Hz), 134.2–128.3 (C$_6$H$_5$), 55.5, 47.9 (NCH), 21.6, 21.3, 20.4, 19.7 (CH$_3$) ppm. ^{31}P{^{1}H} NMR: 78.5 ppm. **3**: IR (CH$_2$Cl$_2$) 2022, 1941, 1900 (ν(CO)), 1613 cm^{-1} (ν(NCO)). ^{1}H NMR (CDCl$_3$, 25 °C): 1.13, 1.20, 1.35, 1.44 (d × 4, 12 H, CH$_3$), 3.69, 5.31 (h × 2, 2 H, NCH), 7.34–7.68 (m, 15 H, C$_6$H$_5$) ppm. ^{13}C{^{1}H} NMR: 219.8 (s), 218.5 (d, CO, J(PC) = 10.7 Hz), 202.9 (d, CO, J(PC) = 58.6 Hz), 187.6 (NCO, J(PC) = 5.3 Hz), 134.2–128.2 (C$_6$H$_5$), 55.5, 49.8 (NCH), 20.9, 20.8, 20.5, 20.4 (CH$_3$) ppm. ^{31}P{^{1}H} NMR: 10.2 (J(PW) = 227.2 Hz) ppm. **6**: IR (CH$_2$Cl$_2$) 2129, 2078 (ν(CN)), 1876 (ν(CO)), 1608 cm^{-1} (ν(NCO)). ^{1}H NMR (CDCl$_3$, 25 °C): 1.27, 1.45 (d × 2, 12 H, CHCH_3), 2.42, 2.46 (s × 2, 12, 6 H, C$_6$H$_3$CH_3), 3.60, 4.72 (h × 2, 2 H, NCH), 7.06 (m, 9 H, C$_6$H$_3$) ppm. ^{13}C{^{1}H} NMR: 242.3 (CO), 197.6 (NCO), 184.1, 174.3 (CN), 134.8–127.7 (C$_6$H$_3$), 54.0, 48.7 (NCH), 20.9, 20.7 (NCHCH_3), 20.9, 19.1 (C$_6$H$_3$CH_3) ppm. **7**: IR (CH$_2$Cl$_2$) 2094 (ν(CN)), 1774 (ν(CO)), 1618 cm^{-1} (ν(NCO)). ^{1}H NMR (CDCl$_3$, 25 °C): 1.30 (m, 12 H, CHCH_3), 2.50 (s, 12 H, C$_6$H$_3$CH_3), 3.30, 4.05 (h × 2, 2 H, NCH), 6.12 (s(br), 3 H, H^4(pz)), 6.90–7.83 (m, 12 H, pz + C$_6$H$_3$) ppm. FAB-MS: 729 (M)$^+$, 701 (M − CO)$^+$, 570 (M − CO, CNR)$^+$, 439 (M − CO, 2CNR)$^+$. Full spectroscopic data for the new complexes are also available from the authors (a.hill@ic.ac.uk). The complexes [W(≡CN^{i}Pr$_2$)I(CO)$_3$(PPh$_3$)], [W(η^2-OCN^{i}Pr$_2$)I(CO)$_3$(PPh$_3$)], and [Mo(η^2-OCN^{i}Pr$_2$)(CO)$_2$(η-C$_5$H$_5$)] have also been crystallographically characterized.[8]

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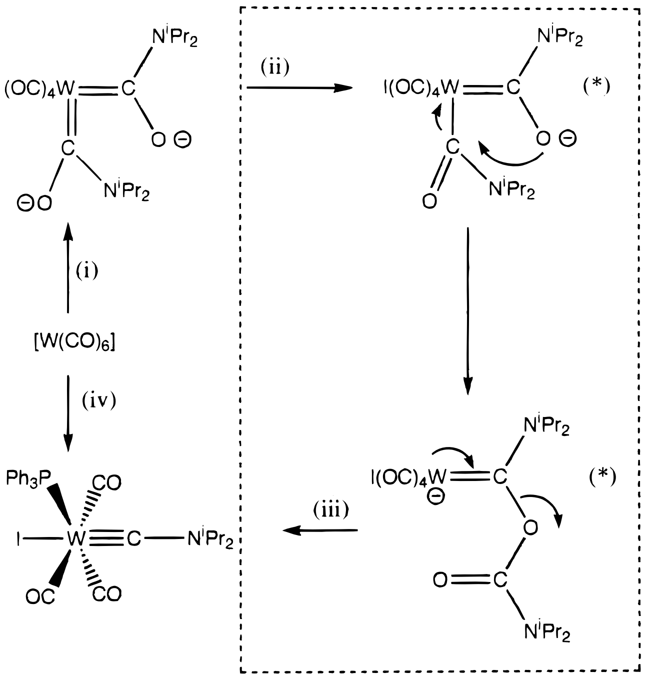
Scheme 3[a]



[a] Reagents and Conditions: (i) 2 LiN^{i}Pr$_2$ (25 °C); (ii) + I$_2$, − LiI (−78 °C); (iii) −LiO$_2$CN^{i}Pr$_2$, + PPh$_3$ (−78 to 25 °C). (iv) LiN^{i}Pr$_2$·LiI, (CF$_3$CO)$_2$O, PPh$_3$. (*) Presumed intermediate, not isolated.

(PPh$_3$)] (**8**) is also obtained. In a similar manner, replacing iodine with bromine provides a chromatographically separable mixture of *fac*-[W(η^2-OCN^{i}Pr$_2$)Br(CO)$_3$(PPh$_3$)] (**9**) and *mer*-[W(≡CN^{i}Pr$_2$)Br(CO)$_3$(PPh$_3$)] (**10**). The yield of **8** appears to be optimized when 1.6 equiv of LiN^{i}Pr$_2$ is used.[10] The formation of **5** is surprising, however, the mechanism shown in Scheme 3 seems to be most plausible to us. This involves the formation of the known bis(carbamoyl)tungstate [W{C(OLi)N^{i}Pr$_2$}$_2$(CO)$_4$],[6a] oxidation of which (by iodine or bromine) initiates the coupling of the two carbamoyl ligands to provide a carbamato−carbene. Subsequently, dissociation of the carbamato substituent then results in formation of the W≡C− multiple bond of **8**. In support of this *intramolecular* mechanism, it should be noted that the *intermolecular* alternative, oxidative cleavage of one carbamoyl ligand as IC(=O)N^{i}Pr$_2$, would produce [W(η^2-OCN^{i}Pr$_2$)I(CO)$_4$], the precursor for **3**. The possibility that the liberated carbamoyl iodide acts as an oxide abstracting agent appears unlikely, given that we have been unable to observe any aminomethylidyne complex formation on treating either [W{C(OLi)N^{i}Pr$_2$}(CO)$_5$] or [W{C(OLi)N^{i}Pr$_2$}$_2$(CO)$_4$] with *N*,*N*-diisopropylcarbamoyl chloride. The process by which **8** is formed from [W{C(OLi)N^{i}Pr$_2$}$_2$(CO)$_4$] is, therefore, mechanistically distinct from the unusual conversion of [Fe(η^2-OCN^{i}Pr$_2$)(CF$_3$)(CO)$_2$(PPh$_3$)] by iodine to [Fe(≡CN^{i}Pr$_2$)(CO)$_3$(PPh$_3$)]I, wherein the trifluoromethyl coligand is essential and intimately involved in the transformation.

The coupling of carbamoyl and aroyl ligands on a platinum center has been previously observed[11] and used to provide insight into the mechanism for palladium catalyzed double-carbonylation reactions which provide α-ketoamides.[12] In a similar manner, bis(alkoxycarbonyl)complexes of divalent iron have been shown to eliminate oxalate esters.[13] These results all involve C−C bond formation in the coupling step. The proposed C−O bond formation in the present example is, therefore, unusual, although we have previously shown that C−O bond formation may occur in the coupling of carbamoyl and difluorocarbene ligands.[14] The above results (i) allow convenient and large scale access to carbamoyl complexes of molybdenum and tungsten and (ii) provide a new rationale for the origin of the “ate” fraction in the Fischer−Tropsch synthesis: Thus acyl ligands may in principle couple and disproportionate to provide surface alkylidyne and carboxylate groups.

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[10] Employing the theoretically requisite 2.0 equiv of LiN^{i}Pr$_2$ leads to intractible mixtures. The complex **8** may be alternatively prepared by the sequential treatment of [W(CO)$_6$] in diethyl ether with LiN^{i}Pr$_2$·LiI, (CF$_3$CO)$_2$O, and PPh$_3$ (40% yield).

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