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

Stephen Anderson, Darren J. Cook, and Anthony F. Hill*

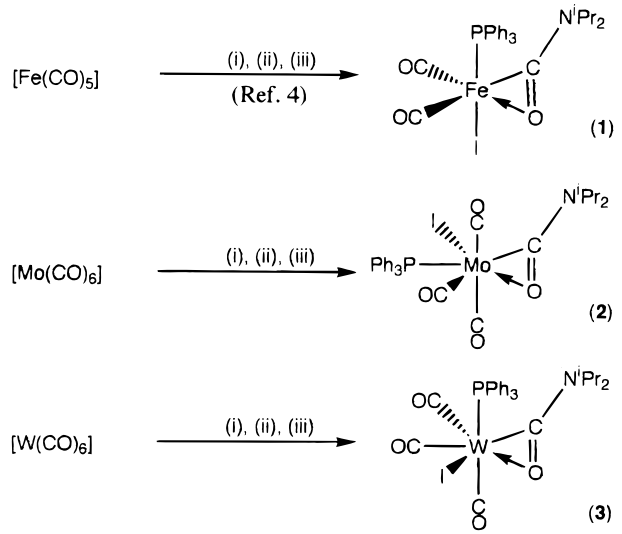
Department of Chemistry, Imperial College of Science Technology and Medicine, South Kensington, London SW7 2AY, U.K.

Received August 18, 1997[⊗]

Summary: Sequential treatment of [M(CO)$_6$] (M = W, Mo, but not Cr) with 1 equiv of LiN^{i}Pr$_2$, iodine, and PPh$_3$ provides [M(η^2-OCN^{i}Pr$_2$)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^{i}Pr$_2$ is employed, the aminomethylidyne complex [W(≡CN-^{i}Pr$_2$)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^{i}Pr$_2$}(CO)$_4$] with (CF$_3$CO)$_2$O and triphenylphosphine has been shown to be solvent dependent: In diethyl ether, the carbamoyl complex [Fe(η^2-OCN^{i}Pr$_2$)(CF$_3$)(CO)$_2$(PPh$_3$)] is obtained,[5] while in dichloromethane the aminomethylidyne salt [Fe(≡CN^{i}Pr$_2$)(CO)$_3$(PPh$_3$)](CF$_3$CO$_2$) is formed.[4] This aminomethylidyne complex has also been unexpectedly obtained from the reaction of [Fe(η^2-OCN^{i}Pr$_2$)(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^{i}Pr$_2$, I$_2$ and PPh$_3$ to provide [Fe(η^2-OCN^{i}Pr$_2$)(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$_2$O; (i) LiN^{i}Pr$_2$, 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^{i}Pr$_2$}(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^{i}Pr$_2$}$_2$(CO)$_4$] with iodine or bromine and triphenylphosphine, which unexpectedly provides the aminomethylidyne complexes [W(≡CN^{i}Pr$_2$)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^{i}Pr$_2$ provides the carbamoyl metalates [M{=C(OLi)N^{i}Pr$_2$}(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^{i}Pr$_2$)I(CO)$_x$] (x = 4, 5, ?); however, if triphenylphosphine is added subsequently, then stable derivatives [M(η^2-OCN^{i}Pr$_2$)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

[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1997.

(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.

(2) Müller, A.; Seyer, U.; Eltzner, W. *Inorg. Chim. Acta*, **1979**, *32*, L65. Müller, A.; Sarkar, S. *Z. Naturforsch., B.* **1978**, *33*, 1053. Ishida, T.; Mizobe, Y.; Tanase, T.; Hidai, M. *Chem. Letts.* **1988**, 441.

(3) Anderson, S.; Hill, A. F. *J. Organomet. Chem.* **1990**, *394*, C24. Anderson, S.; Cook, D. J.; Hill, A. F. *J. Organomet. Chem.* **1993**, *463*, C3.

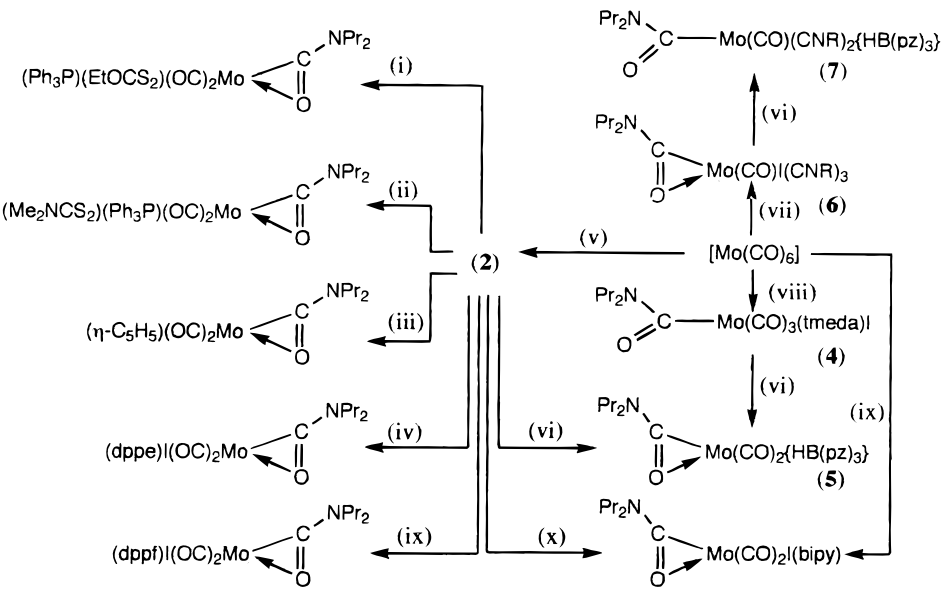
(4) Anderson, A.; Hill, A. F. *Organometallics* **1995**, *14*, 1562.

(5) Anderson, S.; Hill, A. F.; Clark, G. R. *Organometallics* **1992**, *11*, 1990.

(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.

S0276-7333(97)00738-3 CCC: $14.00

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.

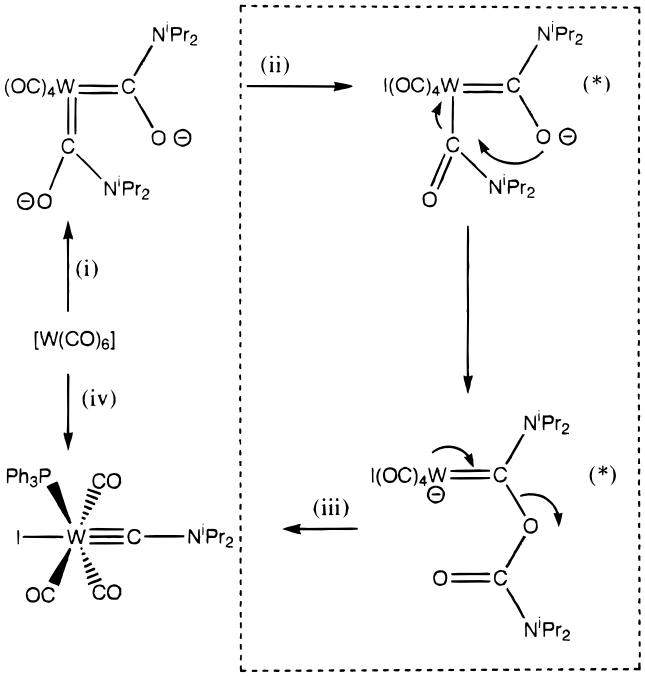
Templeton has shown that the reaction of [Mo(η^2-OCMe)(CO)$_2${HB(pzMe$_2$-3,5)$_3$}] with excess sodium ethoxide results in the formation of the ethylidyne complex [Mo(≡CMe)(CO)$_2${HB(pzMe$_2$-3,5)$_3$}] in 20% yield.[9] A similar reaction ensues between [W(η^2-OCN^{i}Pr$_2$)(CO)$_2$-{HB(pz)$_3$}] 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)$_3$-

(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, CHC*H*$_3$), 2.42, 2.46 (s × 2, 12, 6 H, C$_6$H$_3$C*H*$_3$), 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 (NCH*C*H$_3$), 20.9, 19.1 (C$_6$H$_3$C*H*$_3$) 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, CHC*H*$_3$), 2.50 (s, 12 H, C$_6$H$_3$C*H*$_3$), 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]

(8) Slawin, A. M. Z.; White, A. J. P.; Williams, D. J. Unpublished results.

(9) Brower, D. C.; Stoll, M.; Templeton, J. L. *Organometallics* **1989**, *8*, 2786.

Scheme 3[a]



[a] Reagents and Conditions: (i) 2 LiN^iPr_2 (25 °C); (ii) + I_2, − LiI (−78 °C); (iii) $-LiO_2CN^iPr_2$, + PPh_3 (−78 to 25 °C). (iv) LiN^iPr_2·LiI, $(CF_3CO)_2O$, 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*-$[W(\eta^2\text{-}OCN^iPr_2)Br(CO)_3(PPh_3)]$ (**9**) and *mer*-$[W(\equiv CN^iPr_2)Br(CO)_3(PPh_3)]$ (**10**). The yield of **8** appears to be optimized when 1.6 equiv of LiN^iPr_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 $[W\{C(OLi)N^iPr_2\}_2(CO)_4]$,[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 $IC(=O)N^iPr_2$, would produce $[W(\eta^2\text{-}OCN^iPr_2)I(CO)_4]$, 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 $[W\{C(OLi)N^iPr_2\}(CO)_5]$ or $[W\{C(OLi)N^iPr_2\}_2(CO)_4]$ with *N*,*N*-diisopropylcarbamoyl chloride. The process by which **8** is formed from $[W\{C(OLi)N^iPr_2\}_2(CO)_4]$ is, therefore, mechanistically distinct from the unusual conversion of $[Fe(\eta^2\text{-}OCN^iPr_2)(CF_3)(CO)_2(PPh_3)]$ by iodine to $[Fe(\equiv CN^iPr_2)(CO)_3(PPh_3)]I$, 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.

Acknowledgment. This work was supported by the EPSRC (U.K.). A.F.H. gratefully acknowledges the Royal Society and the Leverhulme Trust for the award of a Senior Research Fellowship.

OM970738Y

(10) Employing the theoretically requisite 2.0 equiv of LiN^iPr_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^iPr_2·LiI, $(CF_3CO)_2O$, and PPh_3 (40% yield).

(11) Huang, T.-M.; Chen, J.-T.; Lee, G.-H.; Wang, Y. *Organometallics* **1991**, *10*, 175.

(12) Ozawa, F.; Yanagihara, H.; Yamamoto, A. *J. Org. Chem.* **1986**, *51*, 415; Ozawa, F.; Soyama, H.; Yanagihara, H.; Aoyama, I.; Takino, H.; Izawa, K.; Yamamoto, A. *J. Am. Chem. Soc.* **1985**, *107*, 3235.

(13) Laurent, P.; Salaun, J. Y.; Legall, G.; Sellin, M.; Desabbayes, H. *J. Organomet. Chem.* **1994**, *466*, 175.

(14) Anderson, S.; Hill, A. F.; Slawin, A. M. Z.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1993**, 266.