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The Synthesis and X-ray Structure of the First Cobalt Carbonyl–NHC Dimer. Implications for the Use of NHCs in Hydroformylation Catalysis

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The synthesis, X-ray structure, and catalytic properties of the first cobalt carbonyl dimer supported by a N-heterocyclic carbene ligand $Co_2(CO)_6(IMes)_2$ {IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene} is reported.

Many comparisons of N-heterocyclic carbenes (NHCs) and organophosphanes (PR_3) have been made in terms of their metal coordination properties, and on this basis their use as possible alternatives for phosphine ligands in homogeneous catalysis has been suggested.[1] Compared to phosphines, NHCs are believed to be strong σ-donors but poor π acceptors and thus may labilize other ligands, while the NHCs themselves are not easily dissociated from the metal center. A consequence of this may be that an excess of ligand is not required to stabilize the catalyst. One such example of industrial importance is hydroformylation where as a result of phosphine degradation (e.g. by P–C bond cleavage[2]) a molar ratio of ligand to metal of >100 is often used. This can be beneficial to catalyst selectivity but is deleterious to catalyst activity and may promote side reactions such as hydrogenation.

Although good progress has been made in the carbene modified rhodium hydroformylation of styrene type olefins, affording high product yields and selectivities,[3] the Rh–carbene hydroformylation of simple α-olefins is, as yet, disappointing in terms of activities and low product linearities.[4] It is generally accepted that better ligands for rhodium hydroformylation are less basic arylphosphines or phosphites[5] and, given the above statements about the nature of the carbene ligand, their poor performance is perhaps not unexpected.

In contrast, basic phosphines are the ligand of choice in cobalt based hydroformylation. Owing to the difficulties associated with rhodium catalyst decomposition in the hydroformylation process of long chain olefins (>C10) for the manufacture of e.g. plasticizer and detergent feedstocks, all commercial plants for these high boiling products currently employ cobalt based hydroformylation.[6] Therefore our group recognizes the importance of maintaining fundamental research in this field,[7] and we have undertaken a study of carbene ligands for cobalt modified hydroformylation.

Only a few cobalt carbene complexes are known. Following the isolation and characterization of the first Fischer-type cobalt carbene complex $[(Ph_3Sn)Co(CO)_3(C(OEt)Ph)]$,[8] a number of other cobalt carbene complexes have been prepared, most of which were stabilized by ligands like nitrosyl[9] and cyclopentadienyl.[10] However, these carbene complexes would not be suitable to serve as precursors for modified cobalt hydroformylation. We now report the synthesis and structure of the first cobalt carbonyl carbene dimer $Co_2(CO)_6(IMes)_2$ **1**.

Literature precedents exist for nucleophilic N-heterocyclic carbenes substituting other ligands such as carbon monox-

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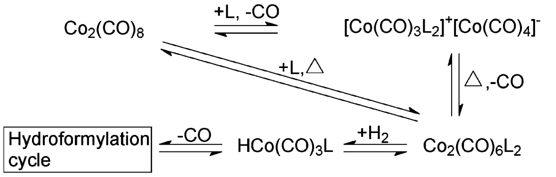
Scheme 1. Catalysts Preforming



ide[11] and phosphines at transition metal centers.[12] It is also well documented that cobalt carbonyl dimers of the type [Co(CO)$_3$P]$_2$ (P = phosphine ligand) can be synthesized from Co$_2$(CO)$_8$ and phosphines at elevated temperatures (Scheme 1).[13]

Taking this into consideration, the free carbene 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene was prepared (from 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride according to literature procedures[14]) and 2 equiv added to a solution of Co$_2$(CO)$_8$ in thf under a CO atmosphere. The disproportionate salt [Co(CO)$_3$(IMes)$_2$]$^+$[Co(CO)$_4$]$^-$ formed within a few minutes and was identified by comparison with previously reported infrared spectra of cobalt phosphine salt derivatives showing a very strong peak at 1886 cm^{-1} [indicative of Co(CO)$_4{}^-$] and 1981 cm^{-1}(mw).[13,15] This behavior is identical to the addition of phosphines to dicobalt octacarbonyl. However, in contrast with most phosphine ligands where the disproportionate salt [Co(CO)$_3$P$_2$]$^+$[Co(CO)$_4$]$^-$ converts to the dimer Co$_2$(CO)$_3$P$_2$ upon heating,[13] the carbene salt did not convert to the dimer even after refluxing for 8 h (Scheme 1). A related observation was made by Lee and Kochi,[15b] who showed that the conversion of the disproportionate ion pair to the corresponding dimer proceeds much more slowly when the phosphine is a stronger σ-donor, e.g., slower for nBu$_3$P than for the PPh$_3$ derivative.

Given this observation, we decided to prepare the target compound indirectly via a cobalt dimer containing a labile ligand, PCyPh$_2$. Thus, addition of PCyPh$_2$ (1.1 equiv) to Co$_2$(CO)$_8$ in thf (25 °C, CO atmosphere) afforded the salt [Co(CO)$_3$(PCyPh$_2$)$_2$]$^+$[Co(CO)$_4$]$^-$ {IR, 1886 cm^{-1} (vs) and 1988 cm^{-1} (ms)}, which converted smoothly to the dimer Co$_2$(CO)$_6$(PCyPh$_2$)$_2$ {IR, 1953 cm^{-1} (vs), 1971 cm^{-1} (w)}[13] at 65 °C. Addition of IMes resulted in the immediate formation of a species with an IR spectrum {1941 cm^{-1} (vs), 1958 cm^{-1} (w) and 1973 cm^{-1} (w)} closely related to the IR spectra of cobalt dimers containing strong σ-donor ligands, e.g., Co$_2$(CO)$_6$(nBu$_3$P)$_2$ {IR (thf), 1943 cm^{-1} (vs), 1962 cm^{-1} (w), and 1984 cm^{-1} (w)},[13] suggesting that this might be the required dimer Co$_2$(CO)$_6$(IMes)$_2$. However, it was not possible to isolate this compound from the reaction mixture due to facile formation of the salt. In an attempt to circumvent this, less-polar solvent systems were evaluated. It was found that addition of IMes in thf to a warm solution (65 °C) of Co$_2$(CO)$_8$ in heptane under a CO blanket (heptane: thf 2:1) resulted in direct formation of Co$_2$(CO)$_6$(IMes)$_2$ **1**. Upon cooling, compound **1** was isolated as dark red crystals of the thf solvate suitable for X-ray diffraction, allowing unequivocal confirmation of the first cobalt carbonyl carbene dimer. **1**·thf is air sensitive and degrades when not stored under a CO atmosphere. Figure 1 shows the molecular structure of **1** with selected bond distances. There is no crystallographic center of symmetry at the Co−Co bond. The bond distance between the Co and the carbene [Co(1)−C(1) = 1.902 Å, Co(2)−C(31) = 1.949 Å] is of the same order as Co−carbene bond distances in previously isolated nitrosyl (1.974 Å)[9] and cyclopentadienyl (1.902 Å)[10] complexes. ^{1}H NMR in d_8-thf only showed one set of signals indicating the symmetrical nature of the dimer in solution.[16]

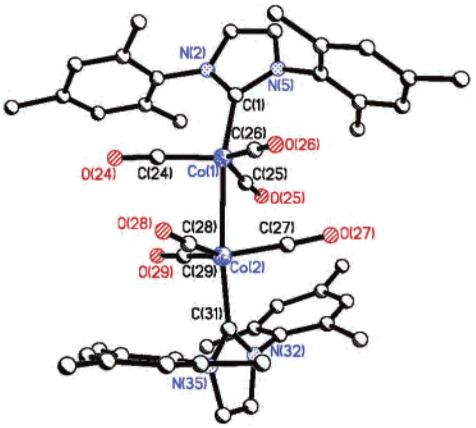


Figure 1. Molecular structure of **1**.[17] Hydrogen atoms omitted for clarity. Selected bond lengths (Å): Co(1)−C(1) 1.902(10), Co(2)−C(31) 1.949(11), Co(1)−Co(2) 2.6973(19).

Compound **1** was tested as a catalyst for the hydroformylation of 1-octene. Co$_2$(CO)$_6$(IMes)$_2$ **1** was prepared in heptane/thf (2:1) and heated under 60 bar of synthesis gas (H$_2$:CO = 2:1) to 170 °C in a 50 mL autoclave. 1-Octene was injected using synthesis gas (2:1) to 85 bar. No gas uptake took place, and GC analysis showed no hydroformylation products. A dark brown oily compound precipitated from the reaction mixture upon cooling. IR of this compound showed a very strong CO band at 1886 cm^{-1} indicative of the [Co(CO)$_4$]$^-$ species. Although this compound has not been unambiguously identified, IR, mass spectroscopy, and NMR data[18] are consistent with it being [1,3-bis(2,4,6-trimethylphenyl)imidazolium]$^+$[Co(CO)$_4$]$^-$ formed by the

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(16) ^{1}H NMR (d_8-thf, 300 MHz): δ 2.1 (s, 24H, 8 × CH$_3$), δ 2.3 (s, 12H, 4 × CH$_3$), δ 7.0 (s, 8H, 8 × ArH), δ 7.24 (s, 4H, 4 × NCH) ppm. ^{13}C NMR (d_8-thf, 100 MHz): δ 15.9 (o-CH$_3$), δ 18.7 (p-CH$_3$), δ 122.7 (NCHCHN), δ 127.1 (Mes C$_{3,5}$), δ 134.3 (Mes C$_{2,6}$), δ 135.7 (Mes C$_4$), δ 136.6 (Mes C$_1$), δ 183.2 (NCN), δ 203.5 (C≡O).

(17) Crystallographic data for **1** (CCDC Number, 218909): Rigaku mercury diffractometer with graphite-monochromated Mo Kα radiation (0.71073 Å), 100 K, empirical formula C$_{52}$H$_{56}$Co$_2$N$_4$O$_7$, M = 966.87, triclinic, space group $P1$, a = 10.811(2) Å, b = 13.080(3) Å, c = 18.794(4) Å, α = 82.83(3)°, β = 74.96(3)°, γ = 70.92(3)°, V = 2423.3(8) Å^3, Z = 2, D_c = 1.325 Mg/m^3, μ = 0.739 mm^{-1}, F(000) = 1012, reflections collected = 12871, independent reflections = 8089 [R(int) = 0.0662], R [$I > 2\sigma(I)$] to give $R1$ = 0.1251 and $wR2$ = 0.3043 for 4271 observed refections, R (all data) to give $R1$ = 0.1879 and $wR2$ = 0.3673.

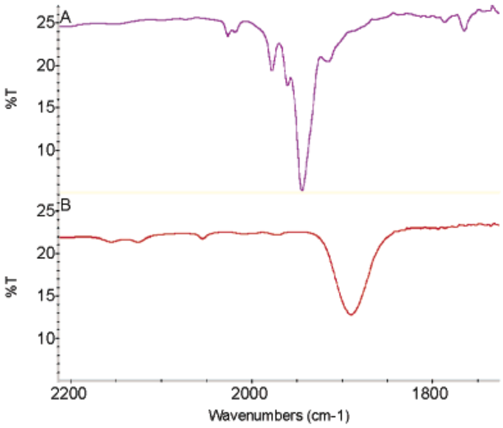

Figure 2. IR traces of compound **1** (A) before and (B) after being subjected to hydroformylation conditions.

reductive elimination of the imidazolium salt H−IMes. Such a reaction has previously been observed by McGuinness et al.[18] in palladium and nickel chemistry. A high-pressure IR experiment was performed by heating a solution of **1** in heptane/thf (2:1) under 60 bar of synthesis gas ($CO:H_2$, 1:1).[19] At 75 °C the dimer started to decompose, and at 100 °C all carbonyl bands collapse to the 1886 cm^{-1} species, confirming the instability of compound **1** (Figure 2). To test the generality of this phenomenom two other carbenes, namely, 1,3-dimethylimidazol-2-ylidene[14] and 1,3,4,5-tetramethylimidazol-2-ylidene,[20] were also evaluated, both affording similar results.

In conclusion, we have synthesized and structurally characterized the first cobalt carbonyl carbene dimer. Although compound **1** appeared to be a perfect candidate for modified cobalt hydroformylation, it was found that this compound was not stable under these hydroformylation conditions.

Supporting Information Available: X-ray crystallographic file (CIF) and tables of crystallographic data for compound **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) (a) ^{1}H NMR (d_8-thf, 300 MHz) of the reaction mixture showed a clear singlet at δ 9.50 (s, NC(H)N). Similar in situ NMR identification of reductive elimination products was done for palladium and nickel complexes of heterocyclic carbenes. (b) McGuinness, D. S.; Cavell, K. J.; Skelton, B. W.; White, A. H. *Organometallics* **1999**, *18*, 1596. (c) McGuinness, D. S.; Saendig, N.; Yates, B. F.; Cavell, K. J. *J. Am. Chem. Soc.* **2001**, *123*, 4029.

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