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Synthesis and Characterization of a Novel Cobalt Carbonyl N-Heterocyclic Carbene Salt. Crystal Structure of $[Co(CO)_3(IMes)_2]^+[Co(CO)_4]^-$

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The disproportionation of dicobalt octacarbonyl induced by the free carbene 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes) and the X-ray characterization of the cyclohexane solvate of the resulting cobalt carbonyl N-heterocyclic carbene salt, $[Co(CO)_3(IMes)_2]^+[Co(CO)_4]^-\cdot 1/4C_6H_{12}$, is reported. The crystal structure represents the first example of a $[Co(CO)_3(L)_2][Co(CO)_4]$ disproportionate salt reported to date.

Carbene ligands, especially those of the imidazolium type, are an increasingly valuable class of ligands in transition-metal compounds and an area of intense research activity.[1] One of the landmark discoveries in this field was the first report of the isolation of a remarkably stable free carbene by Arduengo.[2] Over the past decade several catalytic applications involving carbene ligands have been reported, e.g., olefin metathesis, C−C coupling (Heck, Suzuki, Sonogahira, Stille, etc.), hydrosilylation, benzanellation, and cyclopropanation.[3] Many comparisons of N-heterocyclic carbenes (NHCs) and organophosphanes (PR_3) in terms of their metal coordination electronic properties have been made, and on this basis their use as possible alternatives for phosphine ligands in homogeneous catalysis has been suggested.[3,4] It is widely accepted that carbenes are strong σ-donors but poor π-acceptors and thus may labilize other ligands without dissociation from the metal center and as a result an excess carbene ligand is not required to prevent decomposition of the catalyst. Our interest in hydroformylation[5] encouraged us to look into whether NHC derivatives of Rh and Co could be synthesized and used for the conversion of olefins to aldehydes or alcohols.

Rhodium carbene complexes have been reported for the hydroformylation of styrenic-type olefins affording moderate catalytic activity and good product yield and selectivity.[6] In contrast, we have found that using [Rh(acac)(CO)(L)] (L = 1,3-bis-(2,6-diisopropylphenyl) imidazol-2-ylidene and 1,3-bis-(2,4,6-trimethylphenyl) imidazol-2-ylidene) as catalyst precursor afforded no improved performance in the hydroformylation of 1-hexene than when $[Rh(acac)(CO)_2]$ alone is used.[7] Others have also reported disappointing results for the Rh−carbene hydroformylation of simple α-olefins.[8]

Basic phosphines are the ligands of choice in modified cobalt hydroformylation and therefore based on electronic properties carbenes should be more ideally suited for cobalt-based hydroformylation. Cobalt complexes containing carbene ligands have been known for some time. One of the earliest examples of a Fischer-type cobalt carbene complex was $[(Ph_3Sn)Co(CO)_3(C(OEt)Ph)]$[9] while the first Co(−I) NHC complexes were reported by Lappert[10] followed by

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cyclopentadienyl derivatives.[11] Gibson[12] reported in 2003 the first example of a dicobalt mixed phosphine−carbene complex, $[Co(CO)_3(PPh_3)Co(CO)_3(IMes)]$ via the displacement of two carbonyl ligands from dicobalt octacarbonyl while Llewellyn recently reported the preparation of $[Co(IMes)(CO)_3(Me)]$ by phosphine displacement from the corresponding PPh_3 complex.[13]

It is well documented that cobalt carbonyl dimers of the type $[Co(CO)_3P]_2$ (P = phosphine ligand) can be synthesized from $[Co_2(CO)_8]$ and phosphines.[14] Our group recently showed that a similar approach could be used for the preparation of the equivalent cobalt carbonyl NHC dimer, $[Co(CO)_3IMes]_2$.[15] It is generally accepted that this transformation, particularly in polar solvents, proceeds via ligand-induced dicobalt octacarbonyl disproportionation to produce the Co(I)/Co(−I) salt (eq 1).[16,17]

$$Co_2(CO)_8 + 2L \rightarrow [Co(CO)_3L_2]^+[Co(CO)_4]^- + CO \qquad (1)$$

Upon heating, most disproportionate phosphine salts readily convert to the corresponding homo dimer (eq 2).[14a,18]

$$[Co(CO)_3L_2]^+[Co(CO)_4]^- \rightarrow [Co(CO)_3L]_2 + CO \qquad (2)$$

Interestingly, in nonpolar solvents and at elevated temperatures a direct CO substitution reaction affords the corresponding dimer (eq 3).[14c,16,19]

$$Co_2(CO)_8 + 2L \rightarrow [Co(CO)_3L]_2 + 2CO \qquad (3)$$

In the early 1980s, there was renewed interest in the Co(I)/Co(−I) ionic complex in eq 1 after it had been shown to be a photoactive catalyst precursor in the photochemical hydroformylation of olefins.[20] This resulted in several photochemical studies and proposed radical chain mechanisms involving electron-transfer steps.[21]

The stability of the cobalt carbene disproportionate salt led us to believe it might be possible to isolate this compound as single crystals suitable for X-ray characterization. Although the disproportionate salt was formed almost instantaneously as the major product when THF was used as solvent, we could not manage to isolate crystals from this reaction mixture. However, when IMes (420 mg) dissolved in THF (15 mL) was added to a preheated (65 °C) solution of $[Co_2(CO)_8]$ (210 mg) in heptane (15 mL)/cyclohexane (2 mL), the disproportionate salt and a small amount of the cobalt carbene dimer were detected by solution IR after 30 min. This solution was kept under a blanket of CO and after 3 days at room temperature afforded light yellow needles suitable for X-ray diffraction, allowing unequivocal confirmation of the first cobalt carbonyl NHC disproportionate salt, $[Co(CO)_3(IMes)_2]^+[Co(CO)_4]^-\cdot 1/4C_6H_{12}$.[22] Although the salt was stable in solution under a CO atmosphere, it was air sensitive and degraded when not stored under inert atmosphere.

Surprisingly, despite numerous reports of disproportionate Co(I)/Co(−I)-salts, as far as we are aware, no crystal structure of materials of the kind $[Co(CO)_3(L)_2]^+[Co(CO)_4]^-$ have been reported to date. The report of $[Co(CO)_3(PPh_3)_2]^+PF_6^-$ represents the only example of the cobalt(I)carbonyl cation that has been characterized by X-ray crystallography to date.[23] The disproportionate anion, $[Co(CO)_4]^-$, has been extensively used as a counterion in several isolated compounds, i.e., $[Cp_2Co]^+[Co(CO)_4]^-$ and [*N*-methylquinolinium]$^+$ $[Co(CO)_4]^-$.[24,25] We now report the synthesis and X-ray characterization of the first cobalt carbonyl NHC disproportionate salt, $[Co(CO)_3(IMes)_2]^+[Co(CO)_4]^-\cdot 1/4C_6H_{12}$. The numbering scheme and thermal displacement ellipsoids for the cation and anion are shown in Figure 1.

The compound crystallizes as discrete anion−cation pairs on general positions in the triclinic space group $P\bar{1}$. Each anion−cation pair is accompanied by a cyclohexane solvent molecule situated on an inversion center with an occupation of 50%. The cation displays a severely distorted trigonal bipyramidal geometry with the three CO ligands occupying the equatorial plane and the two carbene ligands in the apical positions. The Co−carbene bond distances are significantly longer than the 1.902(10) and 1.949(11) Å obtained in the $[Co(CO)_3(IMes)]_2$ dimer as reported previously.[15] This

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(22) ^1H NMR (THF-d_8, 300 MHz): 2.0 (s, 24H, 8 × CH_3), 2.5 (s, 12H, 4 × CH_3), 7.0 (s, 8H, 8 × ArH), 7.6 ppm (s, 4H, 4 × NCH); ^{13}C NMR (THF-d_8, 100 MHz): 17.3 (*o*-CH_3), 20.4 (*p*-CH_3), 128.1 (NCHCHN), 129.4 (Mes C3,5), 135.4 (Mes C4), 135.7 (Mes C2,6), 140.0 (Mes C1), 163.1 (NCN), 194.6 ppm (CO).

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(26) Intensity data for $[Co(CO)_3(IMes)_2]^+[Co(CO)_4]^-\cdot 1/4C_6H_{12}$ were collected at 125(2) K on a Bruker SMART CCD diffractometer using graphite-monochromated Mo Kα (0.71073 Å) radiation. Empirical formula: $Co_2\,C_{50.5}\,H_{51}\,N_4\,O_7$; fw: 943.81; T = 125(2) K; crystal system: triclinic; space group: $P\bar{1}$; a = 11.554(2) Å; b = 11.940(2) Å; c = 18.039(3) Å; α = 108.352(3)°; β = 98.820(3)°; γ = 90.829(4)°; V = 2328.9(8) Å^3; Z = 2; μ = 0.768 mm^{-1}; T_{max}/T_{min}, 1.000/0.822; crystal size: 0.19 × 0.10 × 0.01 mm^3; θ limit: 2.41−25.48; index ranges: $-13 \leq h \leq 13$, $-10 \leq k \leq 14$, $-20 \leq l \leq 21$; collected reflections: 14 967; independent reflections: 8362; R_{int}: 0.0443; observed reflections [$I > 2\sigma I$]: 5563; Data/restraints/parameters: 8362/2/599; GOF: 1.016; R1/wR2 ($I > 2\sigma I$): 0.0623/0.1396; R1/wR2 (all data): 0.1081/0.1624; $\Delta\rho_{max}/\Delta\rho_{min}$, 0.942/−0.565 e·Å^{-3}

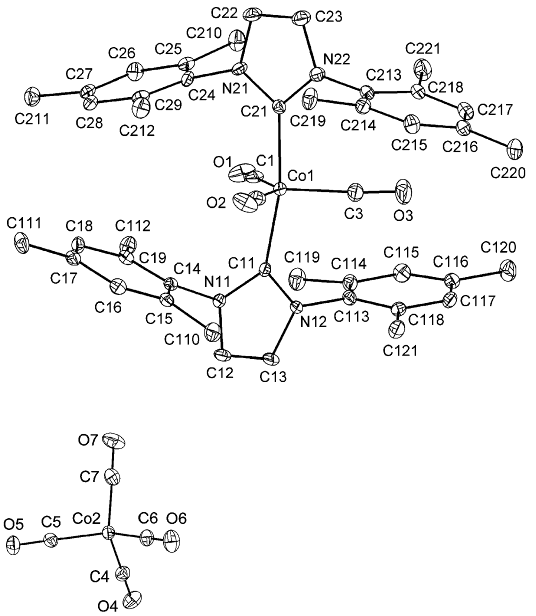

Figure 1. Numbering scheme and thermal ellipsoids (30% probability) for the cation (top) and anion (bottom) in $[Co(CO)_3(IMes)_2]$. $[Co(CO)_4]\cdot 1/4C_6H_{12}$.[26] Hydrogen atoms and the cyclohexane solvent molecule were omitted for clarity. Selected bond lengths (Å) cation: Co1−C11 1.984(4), Co1−C21 1.988(4), Co1−CO_{av} 1.790(6), $(C-O)_{av}$ 1.151(7); anion: Co2-CO_{av} 1.765(6), $(C-O)_{av}$ 1.152(6); and angles (deg) cation: C11−Co1−C21 168.87(17), C1−Co1−C2 141.4(2), C1−Co1−C3 104.7(3), C2−Co1−C3 113.9(3); anion: $(C-Co2-C)_{av}$ 109.5(3).

elongation on the Co−carbene bond distances is most probably due to the large trans influence exerted by the carbene ligands resulting in mutual labilization. The $[Co(CO)_4]^-$ anion displays the expected tetrahedral geometry with all C−Co−C angles close to the ideal case. All equivalent bond distances and angles are similar within the achieved accuracy and are within normal ranges.[27] The Co2−CO bond distances are significantly shorter than the Co1−CO bond distances and may be attributed to the formal negative charge on the anion resulting in more pronounces back-donation to the carbonyl ligands. The C−O bond distances were similar within the level of accuracy for both the anion and cation.

Full crystallographic details for $[Co(CO)_3(IMes)_2][Co(CO)_4]\cdot 1/4C_6H_{12}$ have been deposited with the Cambridge Crystallographic Data Centre, CCDC 628874.

We have found that the best way to prepare the dimer $[Co(CO)_3IMes]_2$ was to circumvent the disproportionate salt formation via using less-polar solvent systems.[15] It was found that addition of 1,3-bis(2,4,6-trimethylphenyl) imidazol-2-ylidene [prepared from 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride according to literature procedures[28] in THF to a warm solution (65 °C) of $[Co_2(CO)_8]$ in heptane (heptane/THF 2:1) resulted in direct formation of $[Co(CO)_3(IMes)]_2$ {IR 1941 (vs), 1958 (w), 1973 cm^{-1} (w)}. When IMes in THF was 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 [indicative of $Co(CO)_4^-$] and 1981 cm^{-1} (vw).[14a,16,18] However, in contrast with most phosphine ligands where the disproportionate salt $[Co(CO)_3P_2]^+[Co(CO)_4]^-$ converts to the $[Co(CO)_3P]_2$ dimer upon heating,[14] the carbene salt did not convert to the dimer even after refluxing for 8 h in THF. A similar observation was made by Lee[16] and Absi-Halabi[21b] who had shown that the formation of the disproportionate ion pair is very fast with strong σ-donor ligands but the conversion of the ionic salt to the corresponding dimer proceeds much slower when containing a strong σ-donor ligand, e.g., $^nBu_3P$, than that for the analogue PPh_3 ion pair. It is reasoned that when L is a strongly electron-donating ligand such as $^nBu_3P$, the potential for oxidation of $[Co(CO)_3L]^\bullet$ is quite high, and thus the quick formation of the disproportionate salt. The same reasoning could apply for the readily formation of the Co−carbene salt.

Unfortunately when either the $[Co(CO)_3(IMes)_2]^+[Co(CO)_4]^-$ salt or the neutral $[Co(CO)_3IMes]_2$ dimer were tested as catalyst precursors for the hydroformylation of 1-octene under commercial conditions (160−170 °C, 80−90 bar H_2/CO 2:1) no catalytic activity was observed.[15] Llewellyn recently evaluated $[Co(IMes)(CO)_3(H)]$ as catalyst precursor for 1-octene hydroformylation under very mild conditions (50 °C, 8 bar syngas) and reported poor activity of ∼43 TON after 17 h (mol product/mol catalyst).[13] We are of the opinion that under harsh hydroformylation conditions irreversible reductive elimination of H-$IMes^+$ results in the formation of $[1,3\text{-bis}(2,4,6\text{-trimethylphenyl})\text{imidazolium}]^+[Co(CO)_4]^-$.[15,29]

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Supporting Information Available: Crystallographic data in CIF format and experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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