Synthesis of Coordinatively Unsaturated Cobalt(II)–Alkyl Complexes Bearing Phosphorus-bridged [1.1]Ferrocenophanes

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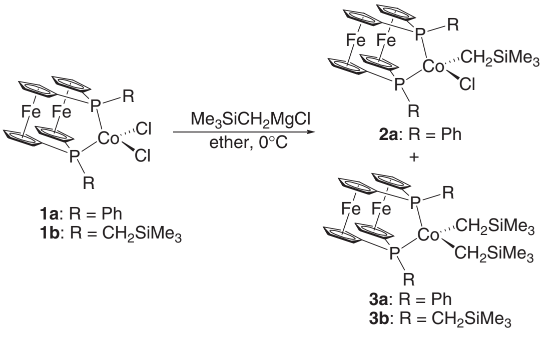
Alkylation of a tetrahedral cobalt(II)–dichloro complex bearing a sterically demanding and electron-donating diphosphine chelate gave a corresponding dialkyl-complex, which is the first coordinatively unsaturated cobalt(II)-(diphosphine)-(dialkyl) complex isolated and characterized by X-ray analysis. This complex is expected to serve as a model intermediate in the cobalt(II)-catalyzed Heck-type reactions.

Coordinatively unsaturated transition-metal-alkyl complexes are important intermediates in stoichiometric and catalytic reactions applied to a variety of substrate-transformations, and it is, therefore, essential to reveal their structures and reactivities, not only to the understanding of these reactions but also to the development of new relevant reactions. However, these metal–alkyl complexes except square-planar d^8 ones are in general labile, and so only a limited number of them have been characterized so far.[1] Recent reports concerning cobalt(II)-catalyzed Heck-type reactions have argued that coordinatively unsaturated cobalt(II)–dialkyl complexes bearing phosphine ligand(s) play a vital role as an intermediate in the catalytic cycle.[2] However, such cobalt(II) complexes are too labile to isolate and/or characterize, whereas some of similar cobalt(II)–diaryl complexes have been found to have a low-spin square-planar structure,[3] and several iron(II)(diphosphine)(diaryl) complexes have been also prepared.[4] We recently established an efficient synthetic route to novel phosphorus-bridged [1.1]ferrocenophanes in which two P atoms are linked doubly with two electron-releasing 1,1′-ferrocenediyl units.[5] Since these bulky diphosphines are expected to exert a peculiar steric demand, an attempt was made in this study to prepare and characterize some of coordinatively unsaturated cobalt(II)–alkyl complexes with these double-chained diphosphines.

Alkylation of the tetrahedral [CoCl$_2$(P-P)] **1a**[5c] bearing PPh-bridged [1.1]ferrocenophane with 2 equivalents of Me$_3$SiCH$_2$MgCl devoid of β-hydrogen atoms in ether, afforded a mixture of mono- and dialkyl complexes **2a** and **3a**, respectively, as precipitates (Scheme 1). Recrystallization from THF/hexane gave a madder crystal of **2a** only. A molecular structure of **2a** was determined by X-ray diffraction[6] to have a distorted tetrahedral geometry (Figure 1). The P–Co–P bite angle of 93.2° was fairly smaller than a tetrahedral angle but was close to that of **1a**, reflecting a steric rigidity of the diphosphine framework.[5] The Co–C bond (2.013(2) Å) was almost comparable to those of a related tetrahedral diamine complex [Co(CH$_2$SiMe$_3$)$_2$(tmeda)] (2.025(7) and 2.024(7) Å) (tmeda = *N,N,N′,N′*-tetramethylethylenediamine).[7]



Scheme 1.

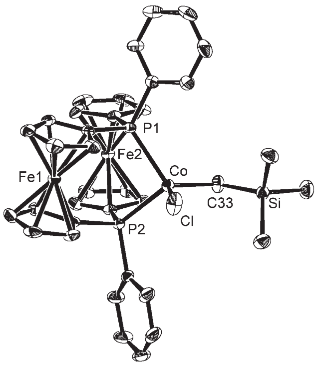


Figure 1. ORTEP drawing of **2a**. Selected bond lengths (Å) and angles (°): Co–Cl 2.2588(7), Co–P1 2.3873(6), Co–P2 2.3742(6), Co–C33 2.013(2); Cl–Co–P1 109.28(3), Cl–Co–P2 108.36(3), Cl–Co–C33 114.43(7), P1–Co–P2 93.15(2), P1–Co–C33 115.30(8), P2–Co–C33 114.26(7).

Any attempts to obtain a single crystal of the dialkyl complex [CoR$_2$(P-P)] **3a** were unsuccessful, but it could be characterized, though paramagnetic, on the basis of ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum of **3a** was quite simple, having only eight resonance signals.[8] Seven of the eight signals appeared at similar positions to those of the precursor complex **1a**,[9] indicating that **3a** would also adopt a tetrahedral geometry. The chemical shift of the eighth signal was observed newly at 9.7 ppm (18H, $\Delta\nu_{1/2} = 100$ Hz) due to the CH$_2$Si*Me*$_3$ groups.[10] The protons on the α-carbon of the C*H*$_2$SiMe$_3$ groups were not observed owing to the paramagnetic cobalt center near-by.

In order to manage to establish the molecular structure of the dialkyl complex, the precursor complex was changed to the Me$_3$SiCH$_2$-substituted diphosphine complex **1b**,[11] which is also rigid but exerts a somewhat different steric demand and possesses stronger electron-donating ability than does **1a**. Treatment of **1b** with Me$_3$SiCH$_2$MgCl in ether yielded a bright yellow-green complex **3b** in 83% yield (Scheme 1), the ^{1}H NMR spectrum of which showed a new signal assignable to the CoCH$_2$Si*Me*$_3$

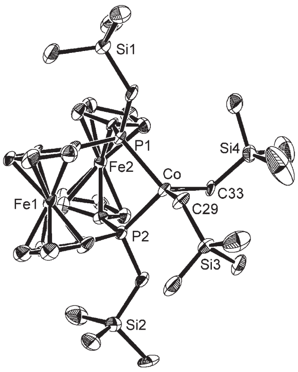


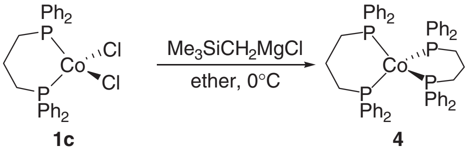
Figure 2. ORTEP drawing of **3b**. Selected bond lengths (Å) and angles (°): Co–P1 2.401(2), Co–P2 2.354(2), Co–C29 2.039(9), Co–C33 2.043(7); P1–Co–P2 92.14(8), P1–Co–C29 112.4(2), P1–Co–C33 117.6(2), P2–Co–C29 117.1(3), P2–Co–C33 105.9(2), C29–Co–C33 110.5(3).

protons at 8.6 ppm (18H, $\Delta\nu_{1/2} = 80$ Hz),[12] together with the signals due to the diphosphine part.

A single-crystal X-ray analysis demonstrates that **3b** is actually our desired dialkyl complex adopting a tetrahedral geometry (Figure 2) and it is the first coordinatively unsaturated cobalt(II)(diphosphine)(dialkyl) complex characterized. It is notable here that the metal center is nicely protected by the two bulky 1,1′-ferrocenediyl units as well as by the methylene groups. The P–Co–P bite angle of 92.1° and the Co–P bond lengths of 2.40 and 2.35 Å are comparable to those of **1a** (95.6°, 2.39 and 2.37 Å)[5c] and of **2a** (vide supra).

For comparison, similar alkylation was conducted on the dichlorocobalt(II) complex bearing a much less bulky but much more flexible dppp ligand (dppp = 1,3-bis(diphenylphosphino)-propane) used often as a supporting chelate in transition-metal catalysts. The reaction of $[CoCl_2(dppp)]$ **1c** with Me_3SiCH_2MgCl in ether afforded a deep-red solution (Scheme 2), which was allowed to stand overnight to give deep-red crystals **4** in 71% yield (based on dppp).[13]

An X-ray analysis revealed **4** to be not an expected cobalt(II)–dialkyl complex but a $[Co^0(dppp)_2]$ complex,[6] which is the first homoleptic cobalt(0)–tetraphosphine complex characterized by X-ray analysis. **4** adopts a distorted tetrahedral geometry with a dppp bite angle of 98.6° and other P–Co–P angles of 102–125°. The Co–P bonds (2.17 Å on average) are much shorter than those of the cobalt(II)–alkyl complexes **3b** and **2a** and other usual Co^{II}–P bonds,[14] which is attributable to an extensive π-back donation from the cobalt(0) center to the P atom(s). Unexpected formation of **4** is probably brought about by the reductive elimination (coupling) of the two alkyl groups on the Co(II) center, followed by the scrambling of the resulting unstable $Co^0(dppp)$ units. In fact, the elimination product $Me_3SiCH_2CH_2SiMe_3$ was detected in the reaction mixture along with some Si-containing by-products by GC-MS analysis. Furthermore, when the reductive elimination takes place, the P–Co–P bite angle of the diphosphine is concomitantly altered so as to facilitate it.[15] It is, therefore, highly plausible that steric bulkiness, rigidity and strong electron-donating ability of the present P-bridged [1.1]ferrocenophanes discourage complexes **3a** and **3b** from undergoing the reductive elimination. Further study regarding the reactivities of **3a** and **3b** is currently underway with particular reference to their catalytic activities.



Scheme 2.

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6 Crystal data for **2a**: $C_{36}H_{37}ClCoFe_2P_2Si{\cdot}C_4H_8O$, triclinic, $P\bar{1}$, $a = 10.1590(2)$, $b = 11.0890(3)$, $c = 17.3800(4)$ Å, $\alpha = 77.854(1)$, $\beta = 75.870(1)$, $\gamma = 86.508(2)°$, $V = 1856.08(8)$ Å^3, $Z = 2$, $D_{calcd} = 1.499$ g cm^{-1}, $T = 200$ K, R/wR factors ($I/\sigma(I) > 3.00$) 0.0346/0.0590, CCDC-288272. Crystal data for **3b**: $C_{36}H_{60}CoFe_2P_2Si_4$, monoclinic, $P2_1/n$, $a = 10.4850(4)$, $b = 21.5770(7)$, $c = 18.6300(4)$ Å, $\beta = 96.870(1)°$, $V = 4184.5(2)$ Å^3, $Z = 4$, $D_{calcd} = 1.330$ g cm^{-1}, $T = 200$ K, R/wR factors ($I/\sigma(I) > 3.00$) 0.0674/0.1248, CCDC-288273. Crystal data for **4**: $C_{54}H_{52}CoP_4$, monoclinic, $C2/c$, $a = 18.247(2)$, $b = 13.138(1)$, $c = 19.919(2)$ Å, $\beta = 110.203(2)°$, $V = 4481.3(7)$ Å^3, $Z = 4$, $D_{calcd} = 1.310$ g cm^{-1}, $T = 294$ K, R/wR factors ($I/\sigma(I) > 3.00$) 0.0344/0.0394, CCDC-288274.

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8 The following ^1H NMR data are reported with the chemical shift followed by the integration, the peak width at half-height in Hertz ($\Delta\nu_{1/2}$) and the peak assignment. ^1H NMR of **3a** (300.4 MHz, C_6D_6, TMS): δ −13.6 (4H, 370 Hz, *o*-Ph), −7.25 (4H, 48 Hz, C_5H_4), −3.61 (2H, 24 Hz, *p*-Ph), 5.55 (4H, 30 Hz, C_5H_4), 6.65 (4H, 30 Hz, *m*-Ph), 9.7 (18H, 100 Hz, $CoCH_2SiMe_3$), 16.2 (4H, 450 Hz, α-C_5H_4), 29.69 (4H, 24 Hz, C_5H_4).

9 ^1H NMR of **1a** (300.4 MHz, $CDCl_3$, TMS): δ −9.6 (4H, 200 Hz, *o*-Ph), −7.00 (4H, 23 Hz, C_5H_4), −2.49 (2H, 15 Hz, *p*-Ph), 5.72 (4H, 15 Hz, C_5H_4), 10.34 (4H, 16 Hz, *m*-Ph), 12.4 (4H, 240 Hz, α-C_5H_4), 26.58 (4H, 10 Hz, C_5H_4).

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11 ^1H NMR of **1b** (300.4 MHz, $CDCl_3$, TMS): δ −8.44 (4H, 26 Hz, C_5H_4), −3.44 (18H, 28 Hz, PCH_2SiMe_3), 4.76 (4H, 20 Hz, C_5H_4), 8.1 (4H, 260 Hz, α-C_5H_4), 27.38 (4H, 7 Hz, C_5H_4).

12 ^1H NMR of **3b** (300.4 MHz, C_6D_6, TMS): δ −4.93 (4H, 46 Hz, C_5H_4), −2.33 (18H, 17 Hz, PCH_2SiMe_3), 4.23 (4H, 22 Hz, C_5H_4), 8.6 (22H, 80 Hz, $CoCH_2SiMe_3$ and α-C_5H_4), 26.86 (4H, 15 Hz, C_5H_4), 43.4 (4H, 390 Hz, PCH_2SiMe_3).

13 ^1H NMR of **4** (300.4 MHz, C_6D_6, TMS): δ 2.7 (160 Hz), 4.0 (70 Hz), 7.7 (150 Hz), 9.68 (19 Hz).

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