

Reduction of terphenyl iron(II) or cobalt(II) halides in the presence of trimethylphosphine: an unusual triple dehydrogenation of an alkyl group†

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The reduction of $\{\text{ArFeBr}\}_2$ (Ar = terphenyl) with KC_8 in the presence of excess PMe_3 afforded the Fe(I) complex $3,5\text{-Pr}^i_2\text{-Ar}'\text{Fe}(\text{PMe}_3)$ (**1**) ($\text{Ar}'\text{-}3,5\text{-Pr}^i_2 = \text{C}_6\text{H-}2,6\text{-}(\text{C}_6\text{H}_3\text{-}2,6\text{-Pr}^i_2)\text{-}3,5\text{-Pr}^i_2$), which has a structure very different from the previously reported, linear Cr(I) species $3,5\text{-Pr}^i_2\text{-Ar}'\text{Cr}(\text{PMe}_3)$ ($3,5\text{-Pr}^i_2\text{-Ar}' = \text{C}_6\text{H-}2,6\text{-}(\text{C}_6\text{H}_2\text{-}2,4,6\text{-Pr}^i_3)_2\text{-}3,5\text{-Pr}^i_2$) and features a strong $\text{Fe-}\eta^6\text{-aryl}$ interaction with the flanking aryl ring of the terphenyl ligand. In sharp contrast, the reduction of $\{\text{ArCoCl}\}_2$ (Ar = $3,5\text{-Pr}^i_2\text{-Ar}'$ and Ar') afforded the allyl complexes $\text{Co}(\eta^3\text{-}\{1\text{-}(\text{H}_2\text{C})_2\text{C-C}_6\text{H}_3\text{-}2\text{-}(\text{C}_6\text{H}_2\text{-}2,4\text{-Pr}^i_2\text{-}5\text{-}(\text{C}_6\text{H}_3\text{-}2,6\text{-Pr}^i_2)\text{-}3\text{-Pr}^i\})\text{-}3\text{-Pr}^i\})\text{(PMe}_3)_3$ (**4**) and $\text{Co}(\eta^3\text{-}\{1\text{-}(\text{H}_2\text{C})_2\text{C-C}_6\text{H}_3\text{-}2\text{-}(\text{C}_6\text{H}_4\text{-}3\text{-}(\text{C}_6\text{H}_3\text{-}2,6\text{-Pr}^i_2)\text{-}3\text{-Pr}^i\})\text{-}3\text{-Pr}^i\})\text{(PMe}_3)_3$ (**5**) formed by an unusual triple dehydrogenation of an isopropyl group. It is proposed that the reduction initially generates an intermediate $3,5\text{-Pr}^i_2\text{-Ar}'\text{Co}(\text{PMe}_3)$, which is similar in structure to **1**, followed by $3,5\text{-Pr}^i_2\text{-Ar}'\text{Co}(\text{PMe}_3)$ decomposition to a cobalt hydride intermediate and dehydrogenation of the isopropyl group *via* remote C–H activation induced by PMe_3 complexation. Complexes **1**, **4**, and **5** were characterized by X-ray crystallography. In addition, **1** was studied by NMR and EPR spectroscopy; **4** and **5** were characterized by NMR spectroscopy.

Introduction

Recent work has shown that a series of dimeric transition metal(I) complexes with the formula $\text{Ar}'\text{MMAr}'$ (M = Cr,¹ Fe² and Co²) could be isolated and characterized with the use of the bulky terphenyl ligand Ar' (Ar' = $\text{C}_6\text{H}_3\text{-}2,6\text{-}(\text{C}_6\text{H}_3\text{-}2,6\text{-Pr}^i_2)_2$). Unlike the $\text{Ar}'\text{CrCrAr}'$ species, which has a quintuple bond between the two Cr centers, the iron and cobalt derivatives have essentially no metal–metal bonding and strong η^6 interactions with one of the flanking $\text{-C}_6\text{H}_3\text{-}2,6\text{-Pr}^i_2$ rings from the terphenyl ligand attached to the neighbouring metal center. By modifying the bulky terphenyl ligand on both the central ring and flanking rings, the monomeric half-sandwich arene complexes ($\eta^6\text{-C}_6\text{H}_6$) $\text{FeAr}'\text{-}3,5\text{-Pr}^i_2$ ³ and ($\eta^6\text{-C}_7\text{H}_8$) $\text{CoAr}'\text{-}3,5\text{-Pr}^i_2$ ⁴ (Ar' $\text{-}3,5\text{-Pr}^i_2 = \text{C}_6\text{H-}2,6\text{-}(\text{C}_6\text{H}_2\text{-}2,4,6\text{-Pr}^i_3)_2\text{-}3,5\text{-Pr}^i_2$) and the inverted sandwich Mn(I) complex ($\mu\text{-}\eta^6\text{-}\eta^6\text{-C}_7\text{H}_8$) $\{\text{MnAr}'\text{-}3,5\text{-Pr}^i_2\}_2$ ³ could be isolated. For chromium, however, the corresponding arene complexes proved to be unstable. Instead the two-coordinate chromium(I) Lewis base complexes $3,5\text{-Pr}^i_2\text{Ar}'\text{Cr}(\text{L})$ (L = THF or PMe_3)⁵ could be obtained upon addition of THF or PMe_3 . We wished to isolate similar Lewis base complexes of univalent later metals such as iron and cobalt in order to obtain two-coordinate M(I) species of the type Ar-M-L (L = donor molecule), which are currently unknown. We now report that the attempted isolation of analogous two-coordinate iron and cobalt complexes leads to the synthesis

and characterization of complexes with very different structures. These are $3,5\text{-Pr}^i_2\text{-Ar}'\text{Fe}(\text{PMe}_3)$ (**1**) ($3,5\text{-Pr}^i_2\text{-Ar}' = 3,5\text{-Pr}^i_2\text{-C}_6\text{H-}2,6\text{-}(\text{C}_6\text{H}_3\text{-}2,6\text{-Pr}^i_2)_2$), which although it has similar stoichiometry to the corresponding two-coordinate Cr(I) complex, has a very strong $\text{Fe-}\eta^6\text{-aryl}$ interaction with a flanking ring from the terphenyl ligand, and the allyl complexes $\text{Co}(\eta^3\text{-}\{1\text{-}(\text{H}_2\text{C})_2\text{C-C}_6\text{H}_3\text{-}2\text{-}(\text{C}_6\text{H}_3\text{-}2,4\text{-Pr}^i_2\text{-}5\text{-}(\text{C}_6\text{H}_3\text{-}2,6\text{-Pr}^i_2)\text{-}3\text{-Pr}^i\})\text{-}3\text{-Pr}^i\})\text{(PMe}_3)_3$ (**4**) and $\text{Co}(\eta^3\text{-}\{1\text{-}(\text{H}_2\text{C})_2\text{C-C}_6\text{H}_3\text{-}2\text{-}(\text{C}_6\text{H}_4\text{-}3\text{-}(\text{C}_6\text{H}_3\text{-}2,6\text{-Pr}^i_2)\text{-}3\text{-Pr}^i\})\text{-}3\text{-Pr}^i\})\text{(PMe}_3)_3$ (**5**), in which the terphenyl ligands have been triply dehydrogenated at an Prⁱ group from a flanking aryl ring to afford η^3 -allyl cobalt phosphine complexes.

Experimental

General procedures

All manipulations were carried out using modified Schlenk techniques under an argon atmosphere or in a Vacuum Atmospheres HE-43 drybox. All of the solvents were first dried by the method of Grubbs,⁶ followed by storage over 3 Å molecular sieves overnight and degassed three times (freeze-thaw) prior to use. $\{3,5\text{-Pr}^i_2\text{-Ar}'\text{FeBr}\}_2$, $\{\text{Ar}'\text{CoCl}\}_2$, and $\{3,5\text{-Pr}^i_2\text{-Ar}'\text{CoCl}\}_2$, were prepared according to a literature procedure.⁷ Melting points were recorded in glass capillaries sealed under N_2 and are uncorrected. UV-vis data were recorded on a Hitachi-1200 spectrometer.

Preparation of $3,5\text{-Pr}^i_2\text{-Ar}'\text{Fe}(\text{PMe}_3)$ (1**).** A pale pink solution of $\{3,5\text{-Pr}^i_2\text{-Ar}'\text{FeBr}\}_2$ (0.926 g, 0.75 mmol) and PMe_3 (0.456 g, 6.00 mmol) in *ca.* 20 mL THF was added dropwise to a freshly prepared suspension of KC_8 (0.203 g, 1.50 mmol) in *ca.* 20 mL THF at 0 °C. The solution turned orange red immediately and was stirred for a further 24 h. The solvent was removed under

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reduced pressure and the resulting dark solid was extracted with hexanes (*ca.* 40 mL). The solution was filtered and the reddish brown filtrate was concentrated to *ca.* 10 mL, which afforded X-ray quality red-brown crystals of **1** after storage for three days at $-18\text{ }^{\circ}\text{C}$. Yield: 0.305 g (33.1%). Melting point: $175\text{--}177\text{ }^{\circ}\text{C}$. UV-vis (hexane, nm [ϵ , $\text{cm}^{-1}\text{M}^{-1}$]): 360 (1800), 426 (850). Anal. calcd For $\text{C}_{39}\text{H}_{58}\text{FeP}$: C 76.33, H 9.53. Found: C 76.51, H 9.69.

Preparation of $\text{Co}(\eta^3\text{-}\{1\text{-(H}_2\text{C)}_2\text{C-C}_6\text{H}_3\text{-2-(C}_6\text{H}_2\text{-2,4-Pr}'_2\text{-5-(C}_6\text{H}_3\text{-2,6-Pr}'_2)\text{-3-Pr}'\})\text{-3-Pr}'\})\text{(PMe}_3\text{)}_3$ (4**).** A dark blue solution of $\{3,5\text{-Pr}'_2\text{-Ar}'\text{CoCl}\}_2$ (1.729 g, 1.50 mmol) and PMe_3 (0.912 g, 12.00 mmol) in *ca.* 30 mL THF was added dropwise to a freshly prepared suspension of KC_8 (0.405 g, 3.00 mmol) in *ca.* 20 mL THF at $0\text{ }^{\circ}\text{C}$. The solution turned orange immediately and stirring was continued for 24 h. The solvent was removed under reduced pressure and the resulting dark solid was extracted with hexanes (*ca.* 60 mL). The solution was filtered and the reddish orange filtrate was concentrated to *ca.* 30 mL and stored in a $-18\text{ }^{\circ}\text{C}$ freezer to afford **4** as X-ray quality orange crystals which were separated from $3,5\text{-Pr}'_2\text{-Ar}'\text{-H}$ produced during reduction. Yield: 0.269 g (11.7%). This compound decomposes to a black solid at $122\text{ }^{\circ}\text{C}$. $^1\text{H NMR}$ (600 M Hz, C_6D_6 , $25\text{ }^{\circ}\text{C}$): $\delta = 1.113$ (d, $^3J_{\text{H-H}} = 6.6$ Hz, 6 H, $\text{CH}(\text{CH}_3)_2$), 1.132 (d, $^3J_{\text{H-H}} = 6.6$ Hz, 6 H, $\text{CH}(\text{CH}_3)_2$), 1.147 (d, $^3J_{\text{H-H}} = 6.6$ Hz, 6 H, $\text{CH}(\text{CH}_3)_2$), 1.162 (d, $^3J_{\text{H-H}} = 6.6$ Hz, 6 H, $\text{CH}(\text{CH}_3)_2$), 1.176 (d, $^3J_{\text{H-H}} = 6.6$ Hz, 6 H, $\text{CH}(\text{CH}_3)_2$), 1.841 (br. m. 9 H, $\text{P}(\text{CH}_3)_3$), 2.543 (s, 2 H, $\text{C}(\text{CH}_2)_2$), 2.620 (s, 2 H, $\text{C}(\text{CH}_2)_2$), 2.729 (sept, $^3J_{\text{H-H}} = 6.6$ Hz, 1 H, $\text{CH}(\text{CH}_3)_2$), 2.750 (sept, $^3J_{\text{H-H}} = 6.6$ Hz, 1 H, $\text{CH}(\text{CH}_3)_2$), 2.780 (sept, $^3J_{\text{H-H}} = 6.6$ Hz, 1 H, $\text{CH}(\text{CH}_3)_2$), 2.801 (sept, $^3J_{\text{H-H}} = 6.6$ Hz, 1 H, $\text{CH}(\text{CH}_3)_2$), 2.852 (sept, $^3J_{\text{H-H}} = 6.6$ Hz, 1 H, $\text{CH}(\text{CH}_3)_2$), 6.830 (s, 1 H, C_6H_2), 7.140 (m, 1 H, $p\text{-C}_6\text{H}_3$), 7.172 (m, 1 H, $p\text{-C}_6\text{H}_3$), 7.311 (m, 2 H, $m\text{-C}_6\text{H}_3$), 7.292 (m, 2 H, $m\text{-C}_6\text{H}_3$), 7.541 (s, 1 H, $o\text{-C}_6\text{H}_2$). $^{31}\text{P NMR}$ (300 M Hz, C_6D_6 , $25\text{ }^{\circ}\text{C}$, ^1H gated decoupled), $\delta = 9.43$ (br. 1 P, PMe_3), -0.05 (br. 2 P, PMe_3). UV-vis (hexane, nm [ϵ , $\text{cm}^{-1}\text{M}^{-1}$]): 387 (4900), 462 (1750).

Preparation of $\text{Co}(\eta^3\text{-}\{1\text{-(H}_2\text{C)}_2\text{C-C}_6\text{H}_3\text{-2-(C}_6\text{H}_4\text{-3-(C}_6\text{H}_3\text{-2,6-Pr}'_2)\text{-3-Pr}'\})\text{-3-Pr}'\})\text{(PMe}_3\text{)}_3$ (5**).** A dark blue solution of $[\text{Ar}'\text{CoCl}]_2$ (1.476 g, 1.50 mmol) and PMe_3 (0.912 g, 12.00 mmol) in *ca.* 30 mL THF was added dropwise to a freshly prepared suspension of KC_8 (0.405 g, 3.00 mmol) in *ca.* 20 mL THF at $0\text{ }^{\circ}\text{C}$. The solution turned orange immediately and was stirred for a further 24 h. The solvent was removed under reduced pressure and the resulting dark solid was extracted with hexanes (*ca.* 60 mL). The solution was filtered and the red orange filtrate was concentrated to *ca.* 15 mL and stored in a $-18\text{ }^{\circ}\text{C}$ freezer. X-ray quality orange crystals were isolated after storage for *ca.* three days at $-18\text{ }^{\circ}\text{C}$. Yield 0.284 g (13.9%). This compound decomposes to a black solid at $117\text{ }^{\circ}\text{C}$. $^1\text{H NMR}$ (300 M Hz, C_6D_6 , $25\text{ }^{\circ}\text{C}$): $\delta = 1.124$ (d, $^3J_{\text{H-H}} = 6.9$ Hz, 6 H, $\text{CH}(\text{CH}_3)_2$), 1.136 (d, $^3J_{\text{H-H}} = 6.9$ Hz, 6 H, $\text{CH}(\text{CH}_3)_2$), 1.140 (d, $^3J_{\text{H-H}} = 6.9$ Hz, 6 H, $\text{CH}(\text{CH}_3)_2$), 1.837 (br. m. 9 H, $\text{P}(\text{CH}_3)_3$), 2.550 (s, 2 H, $\text{C}(\text{CH}_2)_2$), 2.640 (s, 2 H, $\text{C}(\text{CH}_2)_2$), 2.713 (sept, $^3J_{\text{H-H}} = 6.9$ Hz, 1 H, $\text{CH}(\text{CH}_3)_2$), 2.773 (sept, $^3J_{\text{H-H}} = 6.9$ Hz, 1 H, $\text{CH}(\text{CH}_3)_2$), 2.903 (sept, $^3J_{\text{H-H}} = 6.9$ Hz, 1 H, $\text{CH}(\text{CH}_3)_2$), 7.04 (s, 1 H, C_6H_4), 7.113 (m, 1 H, $p\text{-C}_6\text{H}_3$), 7.142 (m, 1 H, $p\text{-C}_6\text{H}_3$), 7.171 (m, 2 H, $m\text{-C}_6\text{H}_3$), 7.192 (m, 2 H, $m\text{-C}_6\text{H}_3$), 7.316 (m, 3 H, C_6H_4). $^{31}\text{P NMR}$ (300 M Hz, C_6D_6 , $25\text{ }^{\circ}\text{C}$, ^1H gated decoupled), $\delta = 9.27$ (br. 1 P, PMe_3), -0.13 (br. 2 P, PMe_3). UV-vis (hexane, nm [ϵ , $\text{cm}^{-1}\text{M}^{-1}$]): 385 (4800), 465 (1600).

Magnetic studies

For a typical measurement, 17.6 mg of **1** was dissolved in exactly 1.0 mL mixture of C_6H_6 and C_6D_6 and some solution was transferred into an NMR tube. Into the NMR tube, a sealed capillary that contained the $\text{C}_6\text{H}_6\text{-C}_6\text{D}_6$ solvent mixture was placed. The NMR spectra were recorded on a Varian spectrometer operating at 300.077 MHz at 292.75 K. Two peaks were identified for C_6H_6 protons, which have a chemical shift difference of 0.231 ppm. Based on the theory of the Evans' method,^{8,9} the magnetic susceptibility was calculated to be $1.92 \times 10^{-3} \text{ cm}^3\text{mol}^{-1}$, which corresponds to an effective magnetic moment of $2.11 \mu_B$ per $3,5\text{-Pr}'_2\text{-Ar}'\text{Fe}(\text{PMe}_3)$ molecule. EPR data were recorded at 8 K on a Bruker EC 106 X-band Spectrometer using an ER-4116 DM dual-mode cavity.

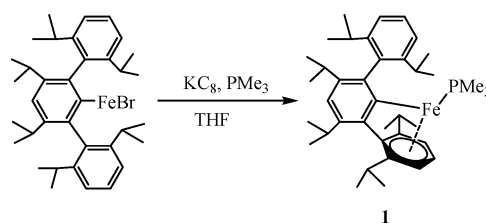
X-Ray crystallography

Suitable crystals of **1**, **4** and **5** were selected and covered with a layer of hydrocarbon oil under a rapid flow of argon. They were mounted on a glass fiber attached to a copper pin and placed in the cold N_2 stream on the diffractometer. X-ray data were collected on a Bruker SMART 1000 diffractometer at $90(2)\text{ K}$ using $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$) or on a Bruker SMART Apex II diffractometer at $90(2)\text{ K}$ with $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$). Absorption corrections were applied using SADABS.¹⁰ The structures were solved using direct methods and refined by the full-matrix least-squares procedure in SHELX.¹¹ All of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions and included in the refinement using a riding model.

Results and discussion

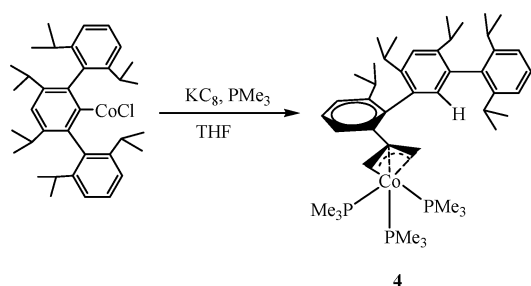
Synthesis

Like the reduction of $\{3,5\text{-Pr}'_2\text{Ar}'\text{CrCl}\}_2$ in the presence of PMe_3 ,⁵ the reduction of $\{3,5\text{-Pr}'_2\text{-Ar}'\text{FeBr}\}_2$ with KC_8 in THF in the presence of excess PMe_3 (Scheme 1) afforded the Fe(I) complex **1**, which has an analogous stoichiometry to the two-coordinate Cr(I) complex. Complex **1** was isolated from hexanes as paramagnetic, air and moisture sensitive dark orange crystals in modest yield.



Scheme 1 Reduction of $\{3,5\text{-Pr}'_2\text{-Ar}'\text{FeBr}\}_2$ with KC_8 in the presence of PMe_3 .

In sharp contrast to **1**, the reduction of $\{3,5\text{-Pr}'_2\text{-Ar}'\text{CoCl}\}_2$ (Scheme 2) under similar conditions did not afford a product analogous to either **1** or the linear $3,5\text{-Pr}'_2\text{Ar}'\text{Cr}(\text{PMe}_3)_5$; instead, the highly unusual conversion of the terphenyl group into an η^3 -allyl ligand was observed and the unexpected product **4** was isolated in low yield after the separation of the co-product



Scheme 2 Reduction of $\{3,5\text{-Pr}^i\text{-Ar}'\text{CoCl}\}_2$ with KC_8 in the presence of PMe_3 .

$3,5\text{-Pr}^i\text{-Ar}'\text{-H}$. The related product **5**, which carries no Pr^i groups on the central aryl ring, was isolated in a similar way.

Structures

The structures of compounds **1**, **4** and **5** were determined by X-ray crystallography. Important data collection and refinement parameters for **1**, **4** and **5** are provided in Table 1.

The structure of **1** is illustrated in Fig. 1. The iron is coordinated to the *ipso* carbon of the aryl ligand and one PMe_3 molecule. Unlike the almost linear two-coordinate $\text{Cr}(\text{I})$ complex $3,5\text{-Pr}^i\text{-Ar}'\text{*Cr}(\text{PMe}_3)$,⁵ the Fe center in **1** has a strongly bent geometry ($\text{C}(1)\text{-Fe}(1)\text{-P}(1) = 113.77(4)^\circ$) with a strong η^6 interaction with one of the flanking $-\text{C}_6\text{H}_3\text{-}2,6\text{-Pr}^i_2$ rings of the terphenyl ligand. The Fe-centroid distance of $1.574(2) \text{ \AA}$, which is slightly longer than the solvent dependent bis(imino)pyridine iron complexes $[2,6\text{-}(2,6\text{-Pr}^i_2\text{-C}_6\text{H}_3\text{N}=\text{CPh})_2\text{C}_3\text{H}_3\text{N}]_2\text{Fe}$ ($1.527(4)$ and $1.534(4) \text{ \AA}$),¹² in which a similar η^6/η^1 interaction was observed. It is similar to those in $[\text{Fe}(\eta^6\text{-C}_{10}\text{H}_8)(1,2\text{-bis(dicyclohexylphosphino)ethane})]$ ($1.597(6) \text{ \AA}$)¹³ and in $\{(\text{C}_6\text{H}_{11}\text{-N}=\text{CH})_2(\eta^6\text{-C}_7\text{H}_8)\text{Fe}\}$ (1.542 \AA).¹⁴ However, it is significantly shorter than those in the terphenyl ligand stabilized monomeric complex $\{(\eta^6\text{-C}_6\text{H}_6)\text{FeAr}'\text{-}3,5\text{-Pr}^i_2\}$ ($1.6427(13) \text{ \AA}$)³ and in the dimeric complex $\{\text{Ar}'\text{FeFeAr}'\}$ ($1.7333(18) \text{ \AA}$).² The terphenyl ligand has a very distorted geometry because of the strong η^6

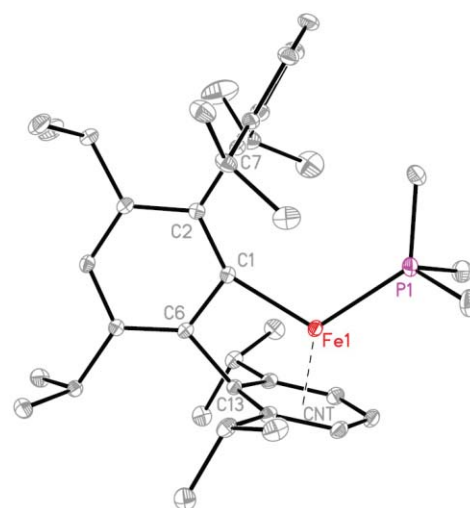


Fig. 1 Molecular structure of **1** with thermal ellipsoids presented at a 30% probability level. All hydrogen atoms are not shown. Selected bond lengths (\AA) and angles ($^\circ$): Fe1-C1 $2.0426(13)$, Fe1-centroid $1.574(2)$, Fe1-P1 $2.2509(5)$, C2-C7 $1.5001(18)$, C6-C13 $1.5122(17)$ Fe-C (flanking ring) $2.0155(13)$, $2.1007(13)$, $2.1027(14)$, $2.1628(14)$, $2.1651(14)$, $2.1679(14)$, C1-Fe1-P1 $113.77(4)$, Fe1-C1-C6 $95.13(8)$, C2-C1-C6 $117.27(11)$, C1-C6-C13 $103.10(11)$, C1-C2-C7 $121.56(12)$.

interaction with the flanking aryl ring; for example, the $\text{Fe}(1)\text{-C}(1)\text{-C}(6)$ and $\text{Fe}(1)\text{-C}(1)\text{-C}(2)$ angles differ by over 42° , the angles involving the flanking rings ($\text{C}(1)\text{-C}(6)\text{-C}(13)$ $103.10(11)^\circ$, $\text{C}(1)\text{-C}(2)\text{-C}(7)$ $121.56(12)^\circ$) differ considerably, and the angle between the $\text{C}(6)\text{-C}(13)$ bond and the interacting aryl ring is *ca.* 143.02° . The C-C bond distances of $\text{C}(13)$ within the flanking ring are on average *ca.* 0.03 \AA longer than the other C-C distance. The strong deviation of $\text{C}(1)\text{-Fe}(1)\text{-P}(1)$ angle from linearity is due to the tendency of the iron, which has a low number of valence electrons (11 without the η^6 -arene interaction), to complex electron rich moieties.¹⁵ The $\text{Fe}(1)\text{-C}(1)$ distance ($2.0426(13) \text{ \AA}$) is essentially the same as those in the aryl $\text{Fe}(\text{I})$ complexes

Table 1 Selected crystallographic data and collection parameters for **1**, **4**, and **5**

| | 1 | 4 | 5 |
|---|--|--|--|
| Formula | $\text{C}_{39}\text{H}_{58}\text{FeP}$ | $\text{C}_{45}\text{H}_{74}\text{CoP}_3$ | $\text{C}_{39}\text{H}_{62}\text{CoP}_3$ |
| Formula weight | 613.67 | 766.88 | 682.73 |
| T/K | 90(2) | 90(2) | 90(2) |
| $\lambda/\text{\AA}$ | 0.71073 | 0.71073 | 0.71073 |
| Colour, habit | Red plate | Orange block | Orange block |
| Crystal system | Monoclinic | Monoclinic | Orthorhombic |
| Space group | $P2_1/n$ | $P2_1/c$ | $Pbca$ |
| $a/\text{\AA}$ | 10.3962(13) | 19.466(3) | 23.347(5) |
| $b/\text{\AA}$ | 15.737(2) | 14.368(3) | 12.992(3) |
| $c/\text{\AA}$ | 22.311(3) | 16.471(3) | 26.446(5) |
| $\alpha/^\circ$ | 90 | 90 | 90 |
| $\beta/^\circ$ | 95.490(2) | 106.466(3) | 90 |
| $\gamma/^\circ$ | 90 | 90 | 90 |
| $V/\text{\AA}^3$ | 3633.6(8) | 4417.7(13) | 8021(3) |
| Z | 4 | 4 | 8 |
| $D_{\text{calcd}}/\text{Mg m}^{-3}$ | 1.122 | 1.153 | 1.131 |
| θ range/ $^\circ$ | 2.75–27.50 | 2.60–25.25 | 2.81–27.49 |
| μ/mm^{-1} | 0.483 | 0.525 | 0.571 |
| Goodness-of-fit on (GOF) F^2 | 1.047 | 0.982 | 1.052 |
| Final R indices [$I > 2\sigma(I)$] | $R_1 = 0.0344$ $wR_2 = 0.0930$ | $R_1 = 0.0585$ $wR_2 = 0.1582$ | $R_1 = 0.0293$ $wR_2 = 0.0774$ |
| Maximum peak/hole/ $e \text{ \AA}^{-3}$ | 0.639/−0.429 | 0.976/−0.604 | 0.474/−0.260 |

$[\eta^6\text{-C}_6\text{H}_6\text{FeAr}^*\text{-3,5-Pr}'_2]$ (2.049(4) Å)³ and $\{\text{Ar}'\text{FeFeAr}'\}$ (2.028(4) and 2.048(4) Å).² The Fe–P distance of 2.2509(5) Å lies in the range 2.157 Å to 2.471 Å,¹⁶ observed in numerous iron phosphine complexes. The strong η^6 -arene interaction exhibited by **1** and other putatively low-coordinate late transition metal complexes is supported by calculations.¹⁷

The structures of **4** and **5** are very similar and are shown in Fig. 2 and 3. The cobalt is no longer bound to the *ipso*

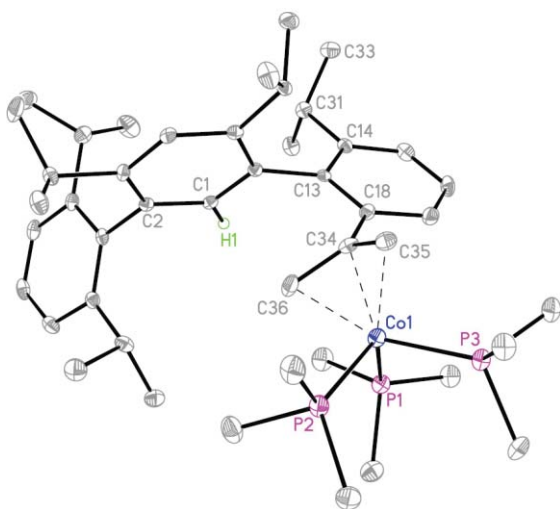


Fig. 2 Molecular structure of **4** with thermal ellipsoids presented at a 30% probability level. All hydrogen (except hydrogen of the central aryl ring) atoms are not shown. Selected bond lengths (Å) and angles (°): Co1–C34 1.974(4), Co1–C35 2.034(4), Co1–C36 2.037(4), Co1–P 2.1405(12), 2.1564(12), 2.1756(12), C18–C34 1.492(5), C14–C31 1.523(5), C31–C33 1.531(5), C34–C36 1.420(5), C34–C35 1.426(5), P1–Co1–P2 108.28(5), P1–Co1–P3 98.70(5), P2–Co1–P3 99.65(5), C18–C34–C36 124.1(4), C18–C34–C35 124.7(3), C35–C34–C36 111.2(3).

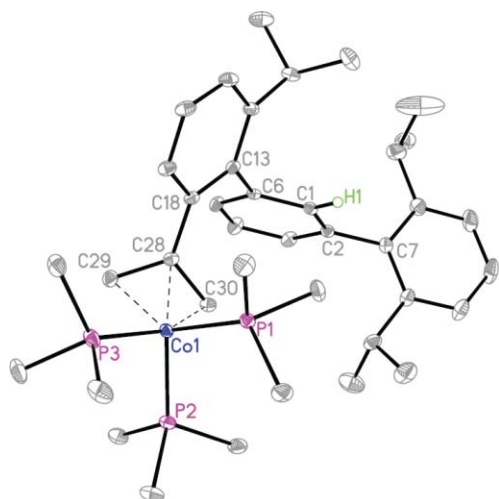
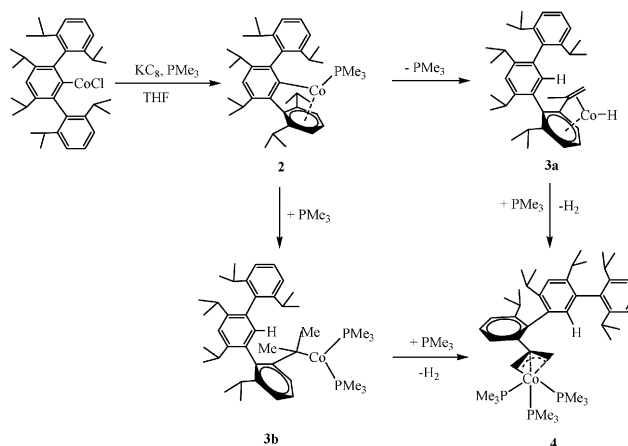


Fig. 3 Molecular structure of **5** with thermal ellipsoids presented at a 30% probability level. All hydrogen (except hydrogen of the central aryl ring) atoms are not shown. Selected bond lengths (Å) and angles (°): Co1–C28 1.9829(15), Co1–C29 2.0395(16), Co1–C30 2.0537(16), Co1–P 2.1546(6), 2.1637(6), 2.1735(6), C18–C28 1.490(2), C28–C29 1.434(2), C28–C30 1.437(2), P1–Co1–P2 106.596(18), P1–Co1–P3 99.174(18), P2–Co1–P3 100.064(19), C18–C28–C29 125.28(14), C18–C28–C30 124.23(14), C29–C28–C30 110.48(13).

carbon of the central ring of the aryl ligand. Instead it becomes coordinated to three carbon atoms that were originally part of an isopropyl group from a flanking aryl ring. The coordination geometry at the central carbon of the allyl group is planar and the C–C distances lie in the range 1.420(5)–1.437(2) Å, consistent with a C–C bond order near 1.5. These distances are slightly longer than bonds in other Co-allyl complexes, such as $\{[(\text{CH}_3\text{O})_3\text{P}](\text{CO})_2\text{Co}[(\text{CH}_2)_2\text{CCH}_2]\}_2(\text{CO})$ (1.408 Å)¹⁸ and $(\eta^3\text{-C}_3\text{H}_5)[\eta^3\text{-2-(CH}_2\text{CH)CH}_2\text{CCH}_2]\text{CoBr}$ (1.394 Å).¹⁹ This may be due to the greater electron density at the metal because of the good σ -donor properties of the PMe_3 co-ligand, which may result in more back donation of electron density into the π^* orbital of the terphenyl ligand. The Co–C distances in **4** and **5** are in the range 1.974(4) Å to 2.0357(16) Å, which is also similar to that observed in the allyl complexes mentioned above and are within the range of Co–C distance of 1.911 to 2.11 Å in allyl cobalt complexes in general.²⁰ The three Co–P distances are uniform with an average Co–P value 2.158(4) Å, which is similar to those in the related complexes $[\textit{anti}\text{-1,2,3,9,10-}\eta^5\text{:4,5,6-}\eta^3\text{-azulene}]\text{Co}_2(\text{PMe}_3)_5$ (2.190(3) Å, average)²¹ and $[\text{Co}(\text{PhCCC}_3\text{H}_{11})(\text{PMe}_3)_3]^+[\text{BPh}_4]^-$ (2.161(2) Å average).²²

We propose that the formation of **4** involves intermediates **2** or **3** (**3a** or **3b**) (see Scheme 3). The similarities of the reduction of $\{\text{Ar}'\text{MX}\}_2$ (M = Fe and Co) in THF² and the reduction of $\{3,5\text{-Pr}'_2\text{-Ar}'\text{MX}\}_2$ in aromatic solvents^{3,4} suggest the initial formation of **2**. This molecule, although it has an 18-electron configuration, is expected to have a geometry more strained than that of **1** owing to the smaller size of cobalt. The strain could lead to cleavage of the Co–C σ -bond of **2** with formation of an alkene/hydride complex **3a** via replacement of the η^1 - PMe_3 ligand by the η^2 -alkene group and concomitant abstraction of two hydrogen atoms from an Pr' group. Under the influence of excess PMe_3 , this intermediate could rearrange to give **4** with elimination of H_2 . This dehydrogenation of inert alkyl groups *via* remote C–H activation has been observed in $\text{Pd}(\text{OAc})_2$ mediated systems,²³ but not for cobalt complexes.



Scheme 3 Proposed mechanisms of the formation of **4**.

A possible alternative mechanism involves the formation of **2** initially. However, it does not involve decomplexation of the PMe_3 ligand. Under the influence of excess PMe_3 , the cobalt center could move to the central carbon atom of the isopropyl group and **3b** could be generated. Upon complexation of a PMe_3 molecule and elimination of H_2 gas, **4** could be formed.

Similarly, reduction of the less bulky ligand stabilized cobalt species $\{\text{Ar}'\text{CoCl}\}_2$ with KC_8 in the presence of excess PMe_3 afforded a similar compound **5**; however, when the reduction was attempted with the significantly smaller $\text{Ar}^\#$ ($\text{Ar}^\# = 2,6\text{-}(2,4,6\text{-Me}_3\text{-C}_6\text{H}_2)\text{-C}_6\text{H}_2$) substituent, which does not have isopropyl groups on the flanking rings, a brown solution was obtained and no product was isolated. Due to the multiple intermediates involved in the reaction, **4** and **5** were isolated in low but reproducible yield.

Magnetic properties of **1**

Both **4** and **5** have 18 electron configurations, but **1** is paramagnetic. According to the Evans' method, the effective magnetic moment is $2.11\mu_B$, which is somewhat larger than the expected spin only value of $1.73\mu_B$ for one unpaired electron. This may be due to orbital contributions.

EPR studies of **1** were undertaken to throw further light on its bonding. The spectrum in Fig. 4 is illustrative of a low-spin d^7 system with the unpaired electron residing in the $3d_{x^2-y^2}$ orbital. This is consistent with the need for the $3d_{z^2}$ orbital to be empty in order to accommodate the lone pair from the phosphine ligand. A slightly rhombic set of g -values was determined [$g_1 = 1.9935$, $g_2 = 2.037$, $g_3 = 2.245$], suggesting that a departure from axial symmetry is induced by the $3,5\text{-}i\text{-Pr}_2\text{-Ar}'$ ligand. Significant hyperfine coupling with a single ^{31}P nucleus is evident given the approximately 28–32 G splitting of doublets observed at each g -value. Their features are satisfactorily simulated using a nearly isotropic A -tensor, [88 85 92] MHz.

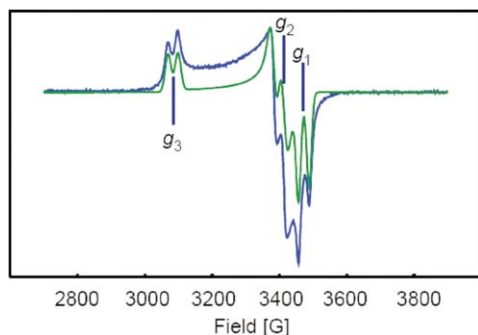


Fig. 4 CW EPR spectra of **1** (blue) and simulation (green) using parameters: $g_1 = 1.9935$, $g_2 = 2.037$, $g_3 = 2.245$. Spectrometer settings: $\nu = 9.6898$ GHz, $T = 8.0$ K, power = 0.19 mW, MF = 100 kHz, MA = 8.0 G, sweep rate = 28.6 G sec^{-1} .

Conclusion

In summary, the Fe(I) complex (**1**) with a geometry very different from its Cr analogue and the allyl Co(I) complexes (**4**) and (**5**) were isolated and characterized. Unlike the two-coordinate chromium species $\text{Ar}^*\text{-}3,5\text{-}i\text{-Pr}_2\text{Cr(L)}$ ($\text{L} = \text{THF}$ or PMe_3),⁵ the

Fe atom in **1** has an η^6 interaction with the flanking aryl ring, which yielded a very distorted geometry due to the tendency of Fe to form arene complexes.¹⁷ In contrast, reduction of $3,5\text{-}i\text{-Pr}_2\text{-Ar}'\text{CoCl}$ and $\text{Ar}'\text{CoCl}$ in the presence of excess PMe_3 afforded the diamagnetic allyl complexes **4** and **5**. The highly unusual formation of **4** and **5** may involve cobalt hydride intermediates and the dehydrogenation of the inert isopropyl group *via* remote C–H activation. The labilities of arene ring and PMe_3 coordination make these compounds attractive substrates for small molecule activation. The study of their chemistry is under way.

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References

- 1 T. Nguyen, A. D. Sutton, M. Brynda, J. C. Fettinger, G. J. Long and P. P. Power, *Science*, 2005, **310**, 844.
- 2 T. Nguyen, W. A. Merrill, C. Ni, H. Lei, J. C. Fettinger, B. D. Ellis, G. J. Long, M. Brynda and P. P. Power, *Angew. Chem., Int. Ed.*, 2008, **47**, 9115.
- 3 C. Ni, B. D. Ellis, J. C. Fettinger, G. J. Long and P. P. Power, *Chem. Commun.*, 2008, 1014.
- 4 H. Lei, B. D. Ellis, C. Ni, F. Grandjean, G. J. Long and P. P. Power, *Inorg. Chem.*, 2008, **47**, 10205.
- 5 R. Wolf, M. Brynda, C. Ni, G. J. Long and P. P. Power, *J. Am. Chem. Soc.*, 2007, **129**, 6076.
- 6 A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen and F. J. Timmers, *Organometallics*, 1996, **15**, 1518.
- 7 A. D. Sutton, T. Ngyuen, J. C. Fettinger, M. M. Olmstead, G. J. Long and P. P. Power, *Inorg. Chem.*, 2007, **46**, 4809.
- 8 D. F. Evans, *J. Chem. Soc.*, 1959, 2003.
- 9 E. M. Schubert, *J. Chem. Educ.*, 1992, **69**, 62.
- 10 *SADABS, version 5.0 package; an empirical absorption correction program from the SAINTPlus NT*, Bruker AXS, Madison, WI, 1998.
- 11 *SHELXL, version 5.1*, Bruker AXS, Madison WI, 1998.
- 12 A. M. Archer, M. W. Bouwkamp, M.-P. Cortez, E. Lobkovsky and P. J. Chirik, *Organometallics*, 2006, **25**, 4269.
- 13 H. Kubo, M. Hirano and S. Komiya, *J. Organomet. Chem.*, 1998, **556**, 89.
- 14 P. Le, Floch, F. Knoch, F. Kremer, F. Mathey, J. Scholz, W. Scholz, K.-H. Thiele and U. Zenneck, *Eur. J. Inorg. Chem.*, 1998, 119.
- 15 P. P. Power, *Chemtracts: Inorg. Chem.*, 1994, **6**, 181.
- 16 The Fe–P distance of iron center to PMe_3 molecule of 118 compounds from Cambridge database (version 5.29, Feb, 2008).
- 17 G. La Macchia, L. Gagliardi, P. P. Power and M. Brynda, *J. Am. Chem. Soc.*, 2008, **130**, 5105.
- 18 K. Cann, P. E. Riley, R. E. Davis and R. Pettitt, *Inorg. Chem.*, 1978, **21**, 1421.
- 19 T. E. Waldman, A. M. Arif and R. D. Ernst, Thesis, 2004 (CCDC 231987).
- 20 The Co–C distance of Co-allyl compounds from Cambridge database (version 5.29, Feb, 2008).
- 21 H.-F. Klein, B. Hammerschmitt, G. Lull, U. Florke and H.-J. Haupt, *Inorg. Chim. Acta*, 1994, **218**, 143.
- 22 A. Bouayad, M. Dartiguenave, M.-J. Menu, Y. Dartiguenave, F. Belanger-Gariepy and A. L. Beauchamp, *Organometallics*, 1989, **8**, 629.
- 23 R. Giri, N. Mangel, B. M. Foxman and J.-Q. Yu, *Organometallics*, 2008, **27**, 1667, and references therein.