Thermally stable coordinatively unsaturated alkyl complexes resistant to β-hydride elimination: Tp^{iPr}M–CH$_2$CH$_3$ (M = Co, Fe)

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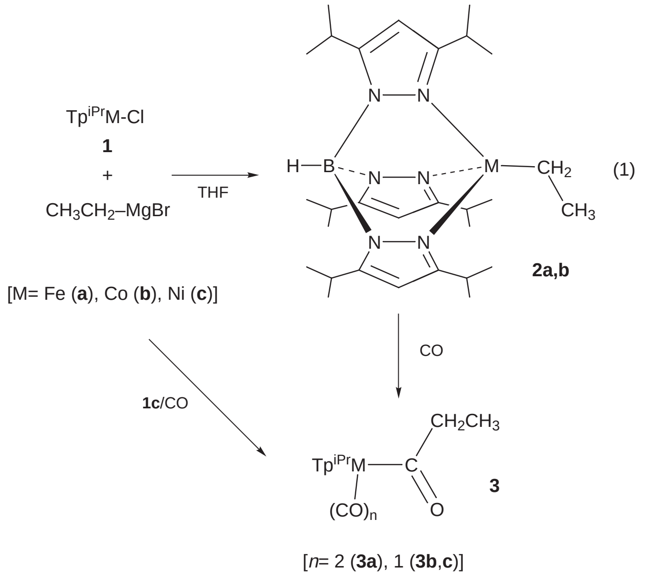
Coordinatively unsaturated hydrocarbyl complexes bearing β-hydrogen atoms, Tp^{iPr}M–CH$_2$CH$_3$ [M = Fe, Co; Tp^{iPr} = hydrotris(3,5-diisopropylpyrazolyl)borate], 14e and 15e species, respectively, are prepared; they are resistant to β-hydride elimination.

'18-Electron (EAN) rule' and 'β-hydride elimination' are usually key principles in predicting stability of organometallic compounds.[1] In a previous paper, we reported a complex which does not obey the 18e rule: the coordinatively unsaturated 14e η^1-allyliron complex supported by the Tp^{iPr} ligand [Tp^{iPr} = hydrotris(3,5-diisopropylpyrazolyl)borate], Tp^{iPr}Fe–CH$_2$-CH=CH$_2$.[2] Although η^3 (π)-coordination of the allyl ligand would give a 16e species, closer to the coordinatively saturated 18e configuration, X-ray crystallography of the allyliron complex revealed that the η^1 (σ)-coordination of the allyl ligand to the iron center led to the highly coordinatively unsaturated 14e species. Our communication was followed by a recent report by Parkin *et al.*, who disclosed the synthesis and unusual reactivity of the related methyliron complex, [PhTp$^{Bu^t}$]Fe–Me [PhTp$^{Bu^t}$ = PhB (3-Bu^t-pz)$_3$, pz = pyrazolyl],[3] and thus the study on the coordinatively unsaturated hydrocarbyl complexes of late transition metals has attracted increasing attention.[4] During the course of our study, we have succeeded in the synthesis and characterization of coordinatively unsaturated alkyl complexes resistant to β-hydride elimination.

Reaction of the Fe and Co chloride complexes **1** with ethylmagnesium bromide in THF afforded pale yellow (**2a**) and blue products (**2b**), respectively, after removal of the inorganic salts by filtration through a Celite pad followed by crystallization from pentane [eqn. (1)]. X-Ray crystallography of the Co complex **2b** [Fig. 1(a)]† revealed the formation of the ethyl complex with tetrahedral coordination geometry as judged by the similar N–Co distances and N–Co–CH$_2$ angles [Co1–N11 2.049(6), Co1–N21 2.017(7), Co1–N31 2.025(7) Å; N11–Co1–C1 123.1(3), N21–Co1–C1 125.2(3), N31–Co1–C1 124.5(3)°]. The Co–CH$_2$ distance [Co1–C1 2.01(1) Å] falls in the accepted range of the Co–C σ-bond lengths. The structural parameters are comparable to those of the allyliron complex mentioned above.[2] The iron complex **2a** was also assigned to Tp^{iPr}Fe–CH$_2$CH$_3$ with tetrahedral structure, on the basis of its cell parameters† similar to those of **2b**, but could not be refined satisfactorily due to the low quality of the crystals. In contrast to the Co and Fe complexes, the reaction of the Ni complex **1c** afforded an intractable mixture of products from which no characterizable product could be isolated.



In order to further confirm the presence of a M–C bond in **2**, the ethyl complexes **2a**,**b** were subjected to carbonylation. Stirring a toluene solution of **2a**,**b** for 1 h under CO atmosphere (1 atm) produced **3a**,**b**, respectively. Their IR spectra containing

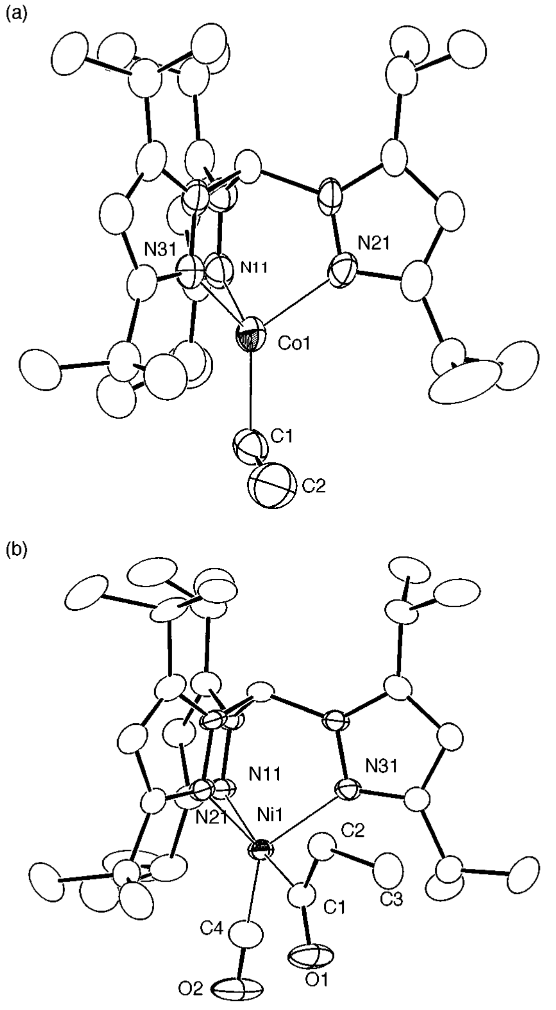


Fig. 1 Molecular structures of **2b** (a) and **3c** (b) drawn at the 30% probability level.

ν(CO) and ν(C=O) vibrations suggest formation of acyl complexes.‡ The diamagnetic iron complex **3a** was characterized on the basis of its ^1H and ^{13}C NMR spectra indicating the $(CO)_2Fe–C(=O)CH_2CH_3$ functional group in addition to the κ^3-Tp^{iPr} ligand, and its IR spectrum suggests the presence of two rotamers as observed for $TpFe(CO)_2–C(=O)CH_3$.[5] The assignment of the monocarbonyl structure of the cobalt complex **3b** is based on the single ν(CO) absorption. Interestingly, although the ethylnickel complex **2c** could not be isolated from the Grignard reaction mentioned above, the reaction under CO atmosphere produced the acyl complex **3c**, which was characterized spectroscopically and structurally [Fig. 1(b)].† The Ni center adopts a trigonal bipyramidal structure with the N11–Ni1–C1 axis, where the κ^3-Tp^{iPr} ligand occupies the two basal and one apical coordination sites and the acyl and CO ligands occupy the remaining apical and coordination sites, respectively, as judged by the interligand angles [N11–Ni1–C1 171.7(1) (≈180°); N21–Ni1–C1 89.8(2), N31–Ni1–C1 87.7(1), C1–Ni1–C4 87.2(2), N11–Ni1–N21 85.1(1), N11–Ni1–N31 86.6(1), N11–Ni1–C4 101.1(2)° (≈90°); N21–Ni1–N31 98.9(1), N21–Ni1–C4 131.0(2), N31–Ni1–C4 129.8(2)° (≈120°)]. In accord with this view, the axial N–Ni distance is slightly longer than the equatorial ones [Ni1–N11 2.058(3) Å > Ni1–N21 2.018(3), Ni1–N31 2.034(3) Å]. As for the Ni(CO)–C(=O)Et part, the structure of the acyl part is normal [Ni1–C1 1.947(4), O1–C1 1.192(5) Å; Ni1–C1–O1 124.2(3), Ni1–C1–C2 115.7(3), C1–C2–C3 112.2(4)°], and the CO ligand is coordinated to the Ni center in a typical η^1-fashion [Ni1–C4 1.767(5), O2–C4 1.126(6) Å; Ni1–C4–O2 177.0(4)°]. Thus the successful characterization of the acyl complexes **3** supports the presence of the $M–CH_2CH_3$ functional group in the starting complexes **2**. The formation of the acyl complexes **3** *via* addition and insertion of CO molecules is in contrast to the result of carbonylation of the related iron–alkyl complex, $[PhTp^{Bu^t}]Fe–Me$, giving the Fe(I) carbonyl complex, $[PhTp^{Bu^t}]Fe–CO$.[3] The difference may arise from the highly sterically demanding $PhTp^{Bu^t}$ ligand, which would hinder formation of penta- or hexa-coordinated species leading to the acyl structure.

When the ethyl complexes **2a**,**b** were heated in heptane for 5 h at 110 °C, only small amounts of ethane [10 (**2a**) and 8% (**2b**) yields] were detected together with trace amounts of ethene by GLC analysis of the gas phase. In contrast, hydrogenolysis (2 atm; 16 h at room temperature) produced ethane in 60 (**2a**) and 91% (**2b**) yields and protonolysis with aqueous HCl afforded ethane in 66 (**2a**) and 96% (**2b**) yields. Thus complexes **2** bearing β-hydrogen atoms were found to be resistant to 'β-hydride elimination'.

The ethyl-iron and -cobalt complexes prepared in the present study are highly coordinatively unsaturated 14e (Fe: **2a**) and 15e species (Co: **2b**), respectively, which are quite sensitive to air and moisture. It is remarkable that, despite their coordinatively unsaturated electronic structures, they are resistant to β-hydride elimination and are stable at room temperature. The magnetic moments [$\mu = 5.0\ \mu_B$ (**2a**), $4.2\ \mu_B$ (**2b**)] close to the calculated spin only magnetic moments [4.90 ($S = 2$), 3.87 ($S = 3/2$)] and EHMO calculations indicate that the ethyl complexes **2** are high spin species and all their non-bonding d-orbitals are fully or half occupied. The stability of the ethyl complexes **2** may be interpreted in terms of the lack of a vacant coordination site (a vacant non-bonding d-orbital)[1] and the high spin electronic configurations should be a result of the tetrahedral coordination geometry regulated by the tripodal Tp^{iPr} ligand. Their electronic structure, however, should be flexible. Upon interaction with an appropriate substrate the electronic configuration may be changed so as to form a vacant coordination site and accommodate a substrate into the coordination sphere as typically exemplified by carbonylation giving the acyl complexes **3**.

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Notes and references

† X-Ray diffraction measurements were made on a Rigaku RAXIS IV imaging plate area detector with graphite-monochromated Mo-Kα radiation. The structures were solved by using the teXsan crystal structure analysis package. *Crystal data*: **2b**: $C_{26}H_{51}N_6BCo$, $M = 553.5$, $T = -60$ °C, monoclinic, space group $P2_1/c$, $a = 10.309(3)$, $b = 16.21(2)$, $c = 19.207(5)$ Å, $\beta = 100.02(2)°$, $V = 3160(4)$ Å^3, $Z = 4$, $D_c = 1.16$ g cm^{-3}, $\mu = 5.7$ cm^{-1}, $R_1 = 0.083$ for the 3267 unique data with $F_o > 4\sigma(F_o)$ and 347 parameters, $wR_2 = 0.224$ for all 4201 unique data.

3c: $C_{31}H_{51}BN_6NiO_2$, $M = 609.3$, $T = -60$ °C, monoclinic, space group $P2_1/n$, $a = 9.968(5)$, $b = 15.820(2)$, $c = 21.570(2)$ Å, $\beta = 97.02(2)°$, $V = 3376(1)$ Å^3, $Z = 4$, $D_c = 1.20$ g cm^{-3}, $\mu = 6.1$ cm^{-1}, $R_1 = 0.084$ for the 5974 unique data with $F_o > 4\sigma(F_o)$ and 431 parameters, $wR_2 = 0.238$ for all 6368 unique data. The disordered C25, C26, C28, C29, C38 and C39 parts were refined taking into account the minor components. CCDC 182/1153. See http://www.rsc.org/suppdata/cc/1999/417/ for crystallographic files in .cif format.

Cell parameters for **2a**: $T = -60$ °C, monoclinic, space group $P2_1/c$, $a = 10.465(4)$, $b = 16.18(1)$, $c = 19.200(8)$ Å, $\beta = 100.87(1)°$, $V = 3193(3)$ Å^3.

‡ *Selected spectral data*: **2a**: 2543 cm^{-1} (ν_{BH}). **2b**: 2541 cm^{-1} (ν_{BH}). **3a**: 2553 (ν_{BH}), 2024, 2000, 1957, 1930 (ν_{CO}), 1668, 1620 cm^{-1} ($\nu_{C=O}$). $\delta_H(CD_2Cl_2)$ 6.39 (2H, 2, pz), 6.36 (1H, s, pz), 3.67 (q, J 7.0 Hz, CH_2). $\delta_C(CD_2Cl_2)$ 259.5 [s, Fe–C(=O)], 215.0 (s, Fe–CO), 56.8 (t, J 130 Hz, CH_2), 10.3 (q, J 128 Hz, CH_2CH_3). **3b**: 2540 (ν_{BH}), 1999 (ν_{CO}), 1636 cm^{-1} ($\nu_{C=O}$). **3c**: 2547 (ν_{BH}), 2009 (ν_{CO}), 1682 cm^{-1} ($\nu_{C=O}$). $\delta_H(CD_2Cl_2)$ 5.84 (3H, s, pz), 1.88 (q, J 7.4 Hz, CH_2), 0.45 (t, J 7.4 Hz, CH_2CH_3). $\delta_C(CD_2Cl_2)$ 225.9 (s, Ni–C(=O)), 187.4 (s, Ni–CO), 40.7 (t, J 132 Hz, CH_2), 11.1 (q, J 127 Hz, CH_2CH_3).

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