14e η^1-Hydrocarbyliron complexes supported by hydrotris(3,5-diisopropylpyrazolyl)borate: the allyl complex prefers a highly coordinatively unsaturated 14e η^1-structure to a 16e η^3-structure‡

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Coordinatively unsaturated allyl and benzyl complexes with the hydrotris(3,5-diisopropylpyrazolyl)borate ligand (Tp^{iPr}), $Tp^{iPr}M$–allyl (M = Ni, Co, Fe) and $Tp^{iPr}Fe$–*p*-methylbenzyl, are prepared and characterized by X-ray crystallography, and the allyl ligand is coordinated to the Fe center in a η^1-fashion to form a 14e species in contrast to the η^3-coordination found for the Ni and Co complexes.

Coordinatively unsaturated organo-transition metal species have attracted much attention, in particular, in connection with catalytic transformations, which require open coordination sites for substrates (*e.g.* 14e species as polymerization catalysts),[1] and electron transfer processes.[2] Although many coordinatively unsaturated early transition metal complexes have been studied, few isolated examples of late transition metal complexes are known.[3] During the course of our study on organometallic complexes supported by the hydrotris(3,5-diisopropylpyrazolyl)borate ligand (Tp^{iPr}),[4]‡ we have found that coordinatively unsaturated hydrocarbyl complexes of the first row, late transition metals are obtained by using the Tp^{iPr} auxiliary. Herein we wish to report synthesis and structural characterization of coordinatively unsaturated hydrocarbyl complexes including a series of allyl complexes, $Tp^{iPr}M$(allyl) (M = Ni, Co, Fe), and a η^1-*p*-methylbenzyliron complex, $Tp^{iPr}Fe$–$CH_2C_6H_4Me$-*p*.[5]

As the first attempts, we examined syntheses of complexes with the allyl ligand, which might stabilize a coordinatively unsaturated species through η^3-coordination. Treatment of the chloride precursors, $Tp^{iPr}MCl$ (M = Ni, Co, Fe), with allylmagnesium chloride in THF afforded the allyl complexes, $Tp^{iPr}M$(allyl) (M = Ni **1**, Co **2**, Fe **3**), after extraction with pentane followed by crystallization (Scheme 1). The diamagnetic Ni complex **1** was stable in the air, whereas the other paramagnetic complexes **2** and **3** should be kept under an inert atmosphere.

The deep red Ni complex **1** was readily assigned to the structure with a η^3-allyl ligand on the basis of its ^{1}H NMR data similar to that of the structurally characterized analogue with the non-substituted Tp ligand,[6]‡ which also indicated occurrence of a dynamic process averaging the three pyrazolyl rings. X-Ray crystallography of **1**§¶ revealed the apparently C_s-symmetrical, square-pyramidal structure with the apical N(31) atom. The structure is similar to those of the Tp derivative[6] and the Co complex (Fig. 1), and distortion toward a square-planar structure is evident from the dissimilar Ni–N distances [Ni–N(11) 1.962(6), Ni–N(21) 1.962(5), Ni–N(31) 2.220(6) Å (difference: 0.26 Å)]. The allyl ligand is coordinated to the Ni center in a η^3-fashion as indicated by the very similar Ni–C distances [Ni–C(1) 1.991(9), Ni–C(2) 2.032(6), Ni(1)–C(3) 2.00(1) Å (difference: 0.04 Å)]. The deep green Co complex **2**§ with similar Co–η^3-allyl-carbon distances [Co–C(1) 2.066(6), Co–C(2) 2.056(4), Co–C(3) 2.077(8) Å] is isostructural with **1** (Fig. 1), though the square-pyramidal character is more evident compared to **1** judging from the smaller difference in the Co–N distances [Co–N(11) 1.983(4), Co–N(21) 1.995(4), Co–N(31) 2.153(4) Å (difference: 0.17 Å)]. Thus the Ni and Co allyl complexes are characterized as square-pyramidal η^3-allyl complexes with 18e- and 17e-configuration, respectively.

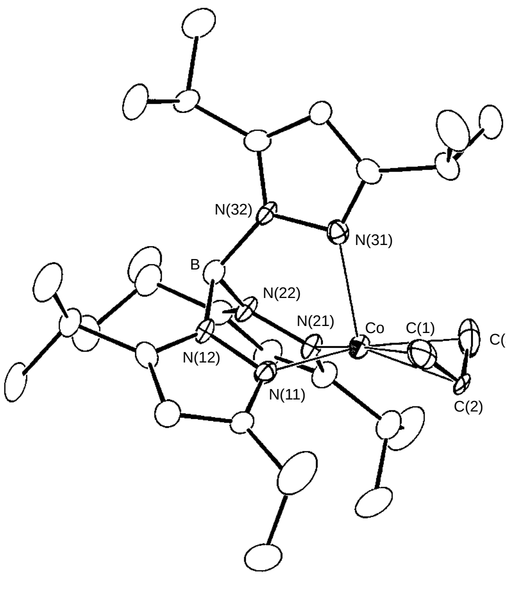
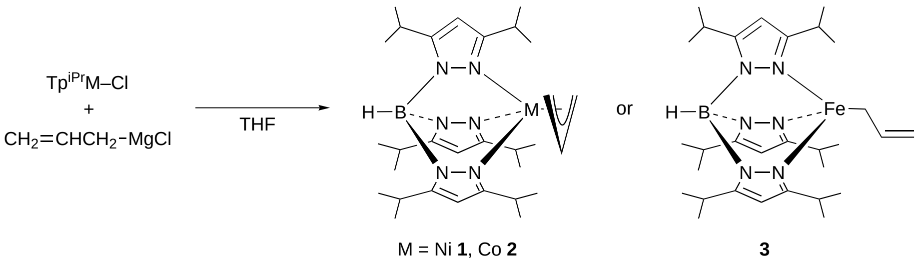


Fig. 1 Molecular structure of **2** drawn at the 30% probability level



Scheme 1

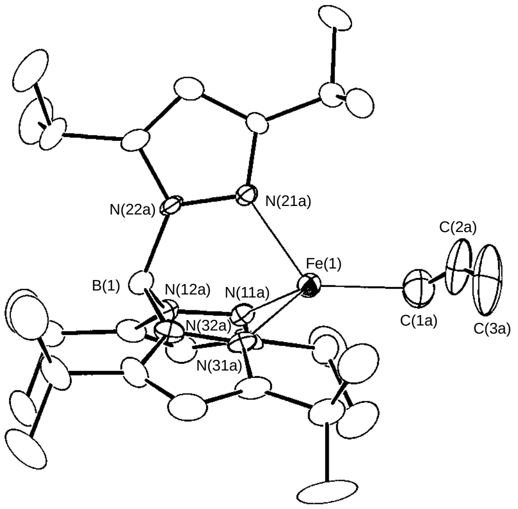


Fig. 2 Molecular structure of **3** drawn at the 30% probability level

The structure of the yellow Fe complex **3** (Fig. 2: two independent molecules)§ is in sharp contrast to those of the Ni and Co complexes. The Fe(1)–C(2a) [2.87(1) Å] and Fe(1)–C(3a) distances [3.75(2) Å] are non-bonding [*cf.* Fe–C(1a) 2.04(1) Å] and, therefore, the allyl ligand is coordinated to the iron center in a η^1-fashion. The iron center adopts a tetrahedral coordination geometry [Fe(1)–N(11a) 2.069(7), Fe(1)–N(21a) 2.071(8), Fe(1)–N(31a) 2.099(9) Å (difference: 0.03 Å)], although a slight deviation from an ideal C_3-symmetrical structure is indicated by the N–Fe(1)–C(1) angles [C(1a)–Fe(1)–N(11a) 119.2(4), C(1a)–Fe(1)–N(21a) 126.5(5); C(1a)–Fe(1)–N(31a) 130.8(6)°]. These structural features lead to the characterization of **3** as a 14e tetrahedral η^1-allyliron complex. Let us point out the curious electronic structure of **3**. If the allyl ligand is coordinated to the iron center in a η^3-fashion (4e-donor), the iron center can receive two more electrons to attain a 16e-configuration closer to coordinative saturation. Such structures are observed for the Ni (**1**) and Co complexes (**2**) with more metal d electrons as mentioned above. Despite this advantage of a η^3-structure, the iron complex with a lower number of d electrons does not adopt the η^3-structure (16e) but the η^1-structure (14e). According to our previous results, the monomeric Tp^RM–X type complexes‡ favor a tetrahedral structure,[7] although X is coordinated through a heteroatom (*e.g.* O, S) with lone-pair electrons, which may stabilize the coordinatively unsaturated metal center through π donation. For **3**, however, such stabilization is not available, and some intrinsic property of the Tp^RM-system may contribute to stabilization of the tetrahedral structures.

The successful isolation of the coordinatively unsaturated hydrocarbyl complex **3** prompted us to examine syntheses of other η^1-hydrocarbyl complexes.[5] As a typical example, the *p*-methylbenzyliron complex, $Tp^{iPr}Fe–CH_2C_6H_4Me$-*p* **4**, was prepared by the Grignard method analogous to Scheme 1, and X-ray crystallography§ revealed a tetrahedral coordination geometry of iron. The structural parameters around the iron center are essentially the same as those of the allyl complex **3** {Fe–C(1) 2.05(1) Å [C(1) is the α-carbon atom of the *p*-methylbenzyl group]; N–Fe–C(1) 116.9(4), 122.7(4), 136.5(4)°}, and slight distortion from a C_3-symmetrical structure is also noted.

In conclusion, coordinatively unsaturated 14e-organoiron complexes including allyl- (**3**) and benzyl-type complexes (**4**) have been synthesized and characterized. Further studies on molecular orbital analysis of the allyl complexes **1**–**3**, synthesis of other hydrocarbyl complexes and reactivity of the obtained hydrocarbyl complexes are now in progress. Preliminary experiments revealed that the η^1-hydrocarbyl complex **4** was readily carbonylated under a CO atmosphere (1 atm) to give the coordinatively saturated dicarbonyl–acyl complex, $Tp^{iPr}Fe(CO)_2C(=O)CH_2C_6H_4Me$-*p* **5**. It is also found that **4** shows reactivity toward unsaturated hydrocarbons, and the results will be reported in due course.

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Notes and References

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‡ Abbreviations used: Tp^{iPr} = hydrotris(3,5-diisopropylpyrazolyl)borate; Tp = hydrotrispyrazolylborate; Tp^R = substituted Tp derivatives.

§ X-Ray diffraction measurements were made on a Rigaku RAXIS IV imaging plate area detector with graphite-monochromated Mo-Kα radiation. The refinements were made on F^2 with SHELXL-93 linked to teXsan. *Crystal data*: **1**: $C_{30}H_{51}BN_6Ni$, M_w = 565.3, T = −60 °C, triclinic, space group $P\bar{1}$, a = 9.778(3), b = 16.76(1), c = 9.720(8) Å, α = 90.348(4), β = 102.87(7), γ = 90.96(7)°, U = 1552(1) Å^3, Z = 2, D_c = 1.21 g cm^{-3}, μ = 6.54 cm^{-1}, $R(R_w)$ = 0.099 (0.121) for the 3648 unique data [$I > 3\sigma(I)$] and 355 parameters. **2**: $C_{30}H_{51}BCoN_6$, M_w = 565.5, T = −60 °C, triclinic, space group $P\bar{1}$, a = 9.733(8), b = 16.818(8), c = 9.718(9) Å, α = 90.88(6), β = 101.59(5), γ = 92.20(5)°, U = 1557(2) Å^3, Z = 2, D_c = 1.21 g cm^{-3}, μ = 5.80 cm^{-1}, $R(R_w)$ = 0.089 (0.107) for the 4644 unique data [$I > 3\sigma(I)$] and 343 parameters. **3** (two independent molecules): $C_{30}H_{51}BFeN_6$, M_w = 562.4, T = −60 °C, orthorhombic, space group $P2_12_12_1$, a = 18.796(2), b = 16.319(2), c = 21.653(4) Å, U = 6642(1) Å^3, Z = 8, D_c = 1.13 g cm^{-3}, μ = 4.80 cm^{-1}, $R(R_w)$ = 0.084 (0.101) for the 4988 unique data [$I > 3\sigma(I)$] and 709 parameters. **4**: $C_{35}H_{55}BFeN_6$, M_w = 626.5, T = −60 °C, triclinic, space group $P\bar{1}$, a = 11.818(9), b = 16.39(1), c = 9.408(4) Å, α = 90.56(4), β = 101.29(4), γ = 91.46(5)°, U = 1786(2) Å^3, Z = 2, D_c = 1.17 g cm^{-3}, μ = 4.53 cm^{-1}, $R(R_w)$ = 0.108 (0.117) for the 2812 unique data [$I > 3\sigma(I)$] and 401 parameters. ORTEP drawings of **1** and **4** are included in supplementary material available upon request from the authors. CCDC 182/804.

¶ The atomic numbering scheme for **1** is the same as that for **2** (Fig. 1) except the metal center.

1 G. W. Coates and R. M. Waymouth, *Comprehensive Organometallic Chemistry II*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon, Oxford, 1995, vol. 12, ch. 12.1; R. F. Jordan, *Adv. Organomet. Chem.*. 1991, **32**, 325; P. W. Dyer, V. C. Gibson, J. A. K. Howard, B. Whittle and C. Wilson, *J. Chem. Soc., Chem. Commun.*, 1992, 1666; K. Mashima, S. Fujikawa, Y. Tanaka, H. Urata, T. Oshiki, E. Tanaka and A. Nakamura, *Organometallics*, 1995, **14**, 2633. See also references cited therein.

2 A leading reference: D. Astruc, *Acc. Chem. Res.*, 1997, **30**, 383.

3 Homoleptic hydrocarbyliron complexes: B. K. Bower and H. G. Tennent, *J. Am. Chem. Soc.*, 1972, **94**, 2512; A. Klose, E. Solari, C. Floriani, A. Chiesi-Villa, C. Rizzoli and N. Re, *J. Am. Chem. Soc.*, 1994, **116**, 9123; R. C. Kerber, *Comprehensive Organometallic Chemistry II*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon, Oxford, 1995, vol. 7, ch. 2.3.1.

4 M. Aktia, K. Ohta, Y. Takahashi, S. Hikichi and Y. Moro-oka, *Organometallics*, 1997, **16**, 4121; Y. Takahashi, M. Akita, S. Hikichi and Y. Moro-oka, *Inorg. Chem.*, in press.

5 Very recently, analogous four-coordinated alkylchromium complexes were reported, though their structures were characterized as *cis*-divacant octahedra in contrast to the tetrahedral structures of the iron complexes **3** and **4**. J. L. Kersten, R. R. Kucharczyk, G. P. A. Yap, A. L. Rheingold and K. H. Theopold, *Chem. Eur. J.*, 1997, **3**, 1668.

6 H. Lehmkuhl, J. Näser, G. Mehler, T. Keil, F. Danowski, R. Benn, R. Mynott, G. Schroth, B. Gabor, C. Kruger and P. Betz, *Chem. Ber.*, 1991, **124**, 441.

7 S. Hikichi, T. Ogihara, K. Fujisawa, N. Kitajima, M. Akita and Y. Moro-oka, *Inorg. Chem.*, 1997, **36**, 4539; M. Ito, H. Amagai, H. Fukui, N. Kitajima and Y. Moro-oka, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 1937; N. Kitajima, T. Katayama, K. Fujisawa, Y. Iwata and Y. Moro-oka, *J. Am. Chem. Soc.*, 1993, **115**, 7872; N. Kitajima and W. B. Tolman, *Prog. Inorg. Chem.*, 1995, **43**, 419.

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