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The first example of a structurally characterized octahedral hydrotris(pyrazolyl)borate iron methyl complex

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Abstract

The one-step synthesis of the known acetyl complex κ^3-TpFe(CO)(PMe_3)(COMe) (**1**, 78% yield) is achieved by reaction of *cis*,*trans*-$Fe(CO)_2(PMe_3)_2MeI$ with potassium hydrotris(pyrazolyl)borate (KTp), in CH_2Cl_2 at room temperature. This reaction is specific to the parent Tp ligand. Visible light irradiation of **1** in toluene for 1 h afforded the first octahedral methyl–iron complex featuring the hydrotris(pyrazolyl)borate ligand TpFe(CO)(PMe_3)Me (**2**) in 80% yield. Compound **2** has been fully characterized by elemental analysis, IR, NMR spectroscopies, cyclic voltammetry and by an X-ray diffraction analysis. A comparison of steric and electronic properties is made with those of related cyclopentadienyl (Cp, Cp*, C_5Ph_5) complexes, and suggests that relative donating abilities follow the trend Cp, Cp*, $C_5Ph_5 >$ Tp, and structural comparisons indicate that Tp is the most sterically demanding ligand.

Keywords: Photochemical decarbonylation; Tris(pyrazolyl)borate; Crystal structure; Alkyl complex; Acyl complex; Iron complex

1. Introduction

Hydrotris(1-pyrazolyl)borate (Tp^-) ligands have often been cited as analogues to cyclopentadienyl (Cp^-) ligands, in that they both typically adopt a facial coordination mode, and act as six-electron donors [1,2]. Nevertheless, the chemistry of the Tp ligand system is not at all as far developed as that of the Cp system. Owing to the differences in size [3] and electronic properties [4], in many cases, unexpected structures and reactivity are observed for these two classes of complexes [5–8]. In particular, organometallic complexes of the type $TpFeL_2X$ still remain scarce, in stark contrast to the abundance of complexes with the $CpFeL_2X$ motif (Cp = substituted or unsubstituted Cp; L = 2-electron neutral donor; X = 2-electron anionic donor) [9]. The known species are mainly acyl-carbonyl compounds TpFe(CO)(L)(COR) (L = CO, PMe_3; R = alkyl or allyl groups). The structurally characterized parent acetyl complex $TpFe(CO)_2(COMe)$ reportedly forms in 8% yield from the reaction of KTp with $Fe_2(CO)_9$ and methyl iodide [10]. The related derivatives *cis*-$TpFe(CO)_2(COCH=CHMe)$ [11], $TpFe(CO)_2(CO$-$C_6H_3Me_2$-2,6) [12] and TpFe(CO)(PMe_3)(COMe) [13] were synthesized from octahedral Fe(II) precursors that were already bearing a σ-Fe–C bond. A third synthetic pathway was reported by Akita and co-workers with the carbonylation of a series of tetrahedral, highly coordinatively unsaturated 14-electron hydrocarbyl complexes Tp^{iPr2}Fe–R, leading to diamagnetic acyl–carbonyl species $Tp^{iPr2}Fe(CO)_2(COR)$ (R = C_2H_5, C_3H_5, *p*-$CH_2C_6H_4Me$, CCPh), [14]. Surprisingly, only three octahedral dicarbonyl complexes with σ-Fe–C bonds, namely $TpFe(CO)_2C_3F_7$ [15], *trans*-$TpFe(CO)_2(CH=CHMe)$ [11], and the unusual ferraoxetene complex TpFe(=C(N*i*Pr_2)OCF_2)CO) [16], have been isolated. The *trans*-vinyl complex resulted from a thermal decarbonylation of its *cis*-propenyl precursor. The cyclometallated derivative resulted from a coupling of carbamoyl and difluorocarbene ligands, and has been crystallographically characterized [16]. Moreover, the

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formation of the transient parent methyl derivative $TpFe(CO)_2Me$ has also been briefly described [17]. In this context, we report here on the high-yield preparation and isolation of the first octahedral iron–methyl complex bearing a hydrotris(pyrazolyl)borato ligand formulated as $TpFe(CO)(PMe_3)Me$, the analytical and spectroscopic characterization (IR, ^1H, ^{13}C and ^{31}P-NMR, cyclic voltammetry) of this chiral molecule, and its X-ray crystal structure. A comparison of the properties of this Fe complex to those based on the analogous CpFe, Cp*Fe and $(C_5Ph_5)Fe$ fragments indicates that the Tp ligand is less electron donating toward iron than the Cp, Cp* and C_5Ph_5 counterparts for this particular half-sandwich series.

2. Results and discussion

2.1. Preparation of $TpFe(CO)(PMe_3)(COMe)$ (**1**)

The reaction of *cis*,*trans*-$Fe(CO)_2(PMe_3)_2MeI$ [18] with potassium hydrotris(pyrazolyl)borate (KTp) in CH_2Cl_2 at room temperature cleanly afforded the known acetyl complexe κ^3-$TpFe(CO)(PMe_3)(COMe)$ (**1**) [13] in 78% yield (Scheme 1).

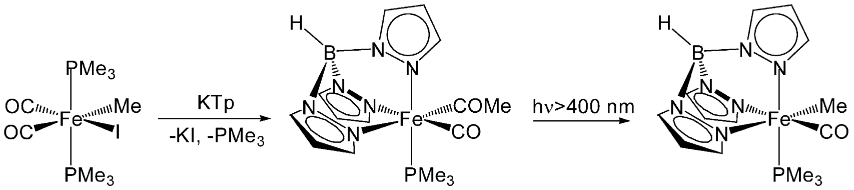
The κ^3-coordination mode is supported by the singlet resonance at δ 28.4 in the $^{31}P\{^1H\}$ NMR spectrum (CD_2Cl_2) of **1**. The analogous bis(phosphine) complex $TpFe(CO)(PMe_3)_2(COMe)$ with a κ^2-Tp ligand has been shown to exhibit a ^{31}P-NMR spectrum with a typical AB spin system [13]. Unfortunately, the ν(B–H) vibration in the infrared spectrum (toluene) was difficult to locate accurately, and thus the criterion based on the B–H vibration frequency [19] could not be used to ascertain the κ^3-coordination mode. The air stable orange acetyl derivative **1** exhibits, however, the expected one strong ν(CO) band at 1943 cm^{-1} for the metal-bonded CO and a less intense ν(CO) band at 1586 cm^{-1} which is attributed to the metal-acyl carbonyl. In the ^1H-NMR spectrum ($CDCl_3$), all the pyrazolyl hydrogen atoms are magnetically inequivalent due to the coordination of the Tp ligand to the stereogenic iron center. All these spectroscopic data are in full agreement with those reported for $TpFe(CO)(PMe_3)(COMe)$ (**1**) by Macchioni and co-workers, who used NaTp as the starting hydrotris(pyrazolyl)borate salt [13].

It is noteworthy that employing KTp directly provided the κ^3-coordination of the Tp ligand. The κ^2-$TpFe(CO)(PMe_3)_2(COMe)$ is indeed the isolated species when the reaction is carried out with NaTp under the same conditions [13]. The κ^3-Tp acetyl derivative **1** is then produced upon refluxing the bidentate intermediate in *n*-hexane for 1 h, during which the third pyrazolyl arm coordinates to the metal while replacing one of the phosphine ligands. A possible mechanism leading to the formation of $TpFe(CO)(PMe_3)(COMe)$ (**1**) implies, as one step, the ionization of the Fe–I bond to generate an iodide salt (KI or NaI). The reaction could then be driven by a salt effect in which a weaker I–K···*N*-pyrazolyl interaction will favor the one-step formation of **1** due to the lower solubility of KI [20]. Such Na^+ versus K^+ salt effects have precedent in the reactivity of organometallic compounds [21].

In our pursuit of tris(pyrazolyl)borate complexes of iron, we have turned our attention to the possibility of employing steric shielding to facilitate the possible formation and/or stabilization of low-coordinate iron complexes. Thus, the above-mentioned procedure has been applied to salts of various $[Tp^R]^-$ anions (Tp^R = Tp*; *t*-$BuB(pz^{R'})_3$; R′ = H, Ph, *i*Pr) [22]. Whatever the MTp^R salts (M = K, Li) and the experimental conditions (time, solvent and temperature) used, the reaction with *cis*–*trans*-$Fe(CO)_2(PMe_3)_2MeI$ failed. The organometallic precursor was always quantitatively recovered as judged by infrared, ^1H and ^{31}P-NMR spectroscopies. This lack of reactivity could result from the increased electronic densities of the $[Tp^R]^-$ anions and/or from intra- and interligand contacts related to steric effects of substituents either at the boron or at the C-3 positions of the pyrazolyl rings [1].

2.2. Preparation of $TpFe(CO)(PMe_3)Me$ (**2**)

Hydrocarbyl complexes can be accessed by thermal [11] or photochemical [23] CO extrusion from their corresponding acyl precursors. As $TpFe(CO)(PMe_3)(COMe)$ (**1**) is thermally stable, having first been generated in boiling *n*-hexane [13], we used the photochemical approach to perform the decarbonylation reaction. Thus, visible light irradiation of compound **1** in toluene for 1 h afforded the desired methyl–iron complex $TpFe(CO)(PMe_3)Me$ (**2**) (Scheme 1). The



Scheme 1.

reaction was monitored by infrared spectroscopy in order to best optimize the formation of **2**. As the photolysis progresses, the original terminal and acetyl CO bands gradually vanish, whereas at the same time one new band, attributable to the methyl compound **2**, appears and progressively becomes more intense at 1912 cm^{-1}. Before the original terminal CO band has completely disappeared, new small bands grow in and the solution becomes more red in color. Evidently, the methyl compound decomposes, giving rise to the homoleptic complex Tp_2Fe [24] which is responsible for the alteration and intensification of the color. This species is easily identified by its characteristic reversible cyclic voltammogram ($E^\circ = -0.23$ V vs. $Cp_2Fe^{0/+}$) [25]. Tp_2Fe is also the only characterizable product of the thermolysis of the aroyl derivative $TpFe(CO)_2(COC_6H_3Me_2$-2,6) [12].

After work-up and crystallization from *n*-hexane, compound **2** is isolated as air and thermally stable, analytically pure orange microcrystals in 80% yield. The compound has been characterized by IR, ^{1}H, ^{13}C, and ^{31}P-NMR spectroscopies (see the Section 4 for details), and by an X-ray diffraction study (vide infra). The IR spectrum (Nujol) displays the characteristic strong terminal carbonyl stretching band at 1912 cm^{-1}, moved to lower frequency than that for the acetyl precursor. The methyl group is a better donor than the acetyl one, improving $Fe(d\pi) \rightarrow CO(\pi^*)$ backbonding which decreases the CO bond order. The ^{1}H-NMR spectrum (CD_2Cl_2) of **2** shows three doublets (H-3), one multiplet (H-5) and three triplets (H-4) which integrate as 1:1:1:3:1:1:1 for the Tp ligand protons. This signal multiplicity is an indication of an asymmetric metal center (i.e. all three pyrazolyl rings are inequivalent with the three Tp (H-5) doublets coincidentally overlapping). The Fe–methyl group appears as a doublet at high field, δ −0.29 ($^3J_{HP} = 4.0$ Hz). The Fe–methyl is also observed in the $^{13}C\{^1H\}$ NMR spectrum as a doublet at δ −5.7 ($^2J_{CP} = 21$ Hz), whereas the Fe–CO ligand resonates at δ 223.2 ($^2J_{CP} = 35$ Hz). The Tp carbon atoms give rise to seven lines, two C-5 and C-4 resonances being isochronous. Finally, the $^{31}P\{^1H\}$ NMR spectrum shows a singlet resonance for the PMe_3 ligand at δ 32.92. Disregarding the facial ligand, the ^{1}H, ^{13}C and ^{31}P-NMR chemical shifts of the remaining three-legged iron moiety are similar to those reported for the closely related complexes $Cp^{\#}Fe(CO)(PMe_3)CH_2R$ ($Cp^{\#}/R = C_5Ph_5/Me$ [23], C_5H_5/H [26], C_5Me_5/H [27]). The results of the spectroscopic analyses clearly lead to the conclusion that structure of the methyl-iron complex $TpFe(CO)(PMe_3)Me$ is best described as a low-spin, octahedral complex. This conclusion is confirmed by the X-ray crystallographic investigation.

2.3. *X-ray crystal structure determination of TpFe(CO)(PMe$_3$)Me (2)*

X-ray quality crystals of $TpFe(CO)(PMe_3)Me$ were grown by slow diffusion of pentane into a saturated dichloromethane solution of **2**. Data from the structural study are presented in the Section 4 (Section 4.3), important bond lengths and angles are depicted in Table 1, and an ORTEP view of the molecular structure of **2** with the atom labeling scheme is presented in Fig. 1. Complex **2** consists of a neutral mononuclear Fe(II) species. The individual molecules of $TpFe(CO)(PMe_3)Me$ are well separated from each other with essentially no intermolecular contact distances of less than the sum of van der Waals radii. Complex **2** crystallizes in the orthorhombic space group P_{bcn}, and the unit cell contains eight molecules.

The methyl and the carbonyl ligands are statistically distributed over two positions and thus precludes any discussions of the exact Fe–C bond lengths. However, the structural analysis clearly establishes that the methyl complex **2** adopts a *pseudo*-octahedral structure, as is invariably observed for six-coordinated TpFe derivatives [10,16,28,29]. The facially coordinated Tp ligand occupies three coordination sites, whereas the methyl and carbonyl carbon atoms and the phosphorus atoms occupy the three remaining sites. The *pseudo*-octahedral coordination environment has the N(1) and P(1) atoms in axial positions, and two pyrazolyl nitrogen atoms (N(3), N(5)) and two carbon atoms (C(10), C(11)) in equatorial positions. The Fe atom is coplanar with these four atoms. In accord with this geometry, the N–Fe–N angles are smaller than the other N–Fe–(C or P) angles. However, the distortion from ideal octahedral coordination geometry is only slight, with mean deviations from ideal angles (90 or 180°) of 1.64 and 3.11°, and with maximum deviations of 3.75 and 3.98°, respectively (see

Table 1
Selected bond lengths (Å) and angles (°) for $TpFe(CO)(PMe_3)Me$ (**2**)

Bond lengths			
Fe(1)–N(1)	2.021(3)	N(1)–N(2)	1.368(3)
Fe(1)–N(3)	2.053(3)	N(3)–N(4)	1.365(4)
Fe(1)–N(5)	2.057(3)	N(5)–N(6)	1.347(5)
Fe(1)–P(1)	2.2395(12)	N(2)–B(1)	1.547(4)
N(4)–B(1)	1.565(5)	N(6)–B(1)	1.534(5)
Bond angles			
C(11)–Fe(1)–C(10)	89.64(16)	N(3)–Fe(1)–N(5)	88.11(11)
C(10)–Fe(1)–N(1)	89.80(14)	N(1)–Fe(1)–P(1)	177.65(7)
C(10)–Fe(1)–N(3)	176.02(14)	N(3)–Fe(1)–P(1)	91.89(8)
C(10)–Fe(1)–N(5)	91.15(15)	N(5)–Fe(1)–P(1)	92.24(8)
C(11)–Fe(1)–N(1)	90.85(13)	N(6)–B(1)–N(2)	107.2(3)
C(11)–Fe(1)–N(3)	90.90(13)	N(6)–B(1)–N(4)	108.2(3)
C(11)–Fe(1)–N(5)	177.01(14)	N(2)–B(1)–N(4)	106.6(3)
N(1)–Fe(1)–N(3)	86.25(10)	C(11)–Fe(1)–P(1)	90.61(12)
N(1)–Fe(1)–N(5)	86.27(10)	C(10)–Fe(1)–P(1)	92.04(13)

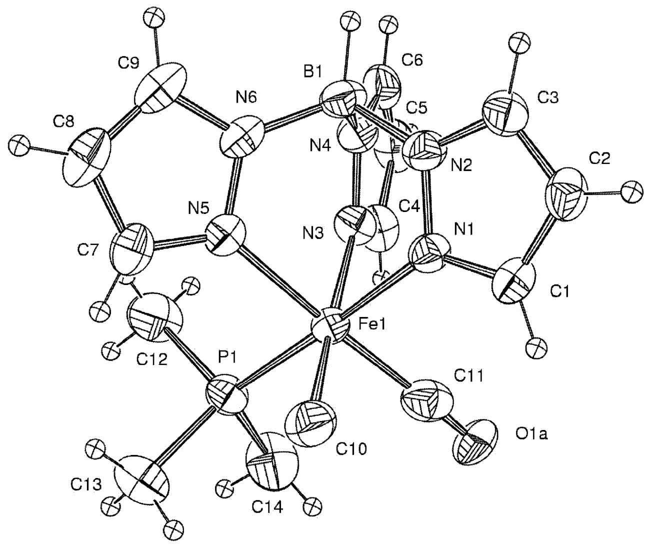


Fig. 1. ORTEP view of TpFe(CO)(PMe_3)Me (**2**) with the atom labeling scheme. Displacement ellipsoids are at the 50% probability level.

Table 1). The axial Fe–N bond distance (2.021(3) Å) is slightly shorter than the two equivalent equatorial Fe–N distances of 2.053(3) and 2.057(3) Å. The Fe–N separation (av. 2.044 Å) is somewhat larger than those determined in the acetyl-iron complex $TpFe(CO)_2$-(COMe) (av. $d_{Fe-N} = 2.024$ Å) [10] and in the ferraoxethane TpFe(CO)(CN*i*Pr_2OCF_2) (av. $d_{Fe-N} = 2.026$ Å) [16]. This is probably due to the sterically more demanding PMe_3 ligand. Likewise, the Fe–P bond distance (2.2395(12) Å) is longer than the lengths measured for other mononuclear complexes with the "$Cp^{\#}$Fe(CO)(PMe_3)(σ-C)" motive (d_{Fe-P} 3/4 2.023 Å) [30]. The Fe–P separation increases with the steric bulk of the facial ligand (Tp > C_5Ph_5 > Cp*, Cp). All the other bond lengths and angles measured in the hydrotris(pyrazolyl)borate ligands are unexceptional (see Table 1).

*2.4. Probes for the electron density at the metal in **1**, **2**, and related complexes*

Cyclic voltammetry experiments indicate a very rapid rearrangement upon oxidation of both TpFe(CO)(PMe_3)(COMe) (**1**) and TpFe(CO)(PMe_3)Me (**2**). In CH_2Cl_2, compound **1** exhibits an irreversible oxidation wave at 0.39 V versus $Cp_2Fe^{0/+}$ at voltage scan rates v of 1–100 V s^{-1}. At $v > 5$ V s^{-1}, a new irreversible wave appeared at 0.07 V during the reverse scan, and is attributed to the reduction of a species resulting from the degradation of the electrode generated short-lived radical cation $\mathbf{1}^{\bullet +}$. The irreversible oxidation wave is also observed in acetonitrile at 0.34 V ($v = 1$ V s^{-1}) but moved to -0.29 V at $v = 100$ V s^{-1} and in this case exhibited partial reversibility ($i_{pc}/i_{pa} = 0.7$, $\Delta E_p = 98$ mV). This behavior sharply contrasts with that of CpFe(CO)(PPh_3)(COMe) which exhibited reversible electrochemical oxidation ($E° = 0.36$ V, $\Delta E_p = 60$ mV, $v = 50$ mV s^{-1} [31]. As expected from the IR spectroscopy data, the methyl derivative **2** is easier to oxidize than its acetyl precursor **1**, and shows an irreversible wave at 0.16 V in its cyclic voltammogram (CH_2Cl_2, $v =$ 1 V s^{-1}), as in the Cp series [31]. At higher scan rate ($v = 50$ V s^{-1}), a partially reversible reduction wave is observed at -0.03 V ($i_{pc}/i_{pa} = 0.7$, $\Delta E_p = 130$ mV), and could arise from the reduction of a solvated acetyl cation radical. A migratory insertion following oxidation of TpFe(CO)(PMe_3)Me might be very rapid, as is observed for the Cp series [31]. In acetonitrile, two irreversible oxidation waves are observed at -0.23 and 0.08 V, at all voltage sweep rates. It is noteworthy that the electron-transfer induced decomposition pathway is quite different from that induced thermally [10–12] or photochemically (vide supra). Indeed, the transient cation radicals $\mathbf{1}^{\bullet +}$ and $\mathbf{2}^{\bullet +}$ never transformed into the bis(hydrotris(pyrazolyl)borate) iron complex on the voltammetric time scale, since the signature of the $Tp_2Fe^{0/+}$ reversible couple [25] was never observed in the recorded cyclic voltammograms.

The v(CO) stretching frequencies of metal-bound carbonyls are a gauge of the electron density of the metal center and thereby of the electron-donating abilities of the ancillary ligands bound to the metal. A comparison of IR data for iron carbonyl complexes featuring the hydrotris(pyrazolyl)borate and cyclopen-

Table 2
Comparative CO stretching frequencies for (FL)Fe(CO)(L)R (FL = Tp, Cp, Cp*; C_5PH_5; L = CO, PMe_3; R = COMe, COEt, Me, Et)

Compound	v(C–O) (cm^{-1})	Reference
$TpFe(CO)_2$(COMe) [a]	2047, 2032, 1987, 1973	[10]
$TpFe(CO)_2$Me [a]	2028, 1968	[10]
TpFe(CO)(PMe_3)(COMe)	1952 [b]	[13]
	1943 [c]	This work
TpFe(CO)(PMe_3)Me [d]	1912	This work
$Tp^{iPr2}Fe(CO)_2$(COEt) [e]	2024, 2000, 1957, 1930	14c
$CpFe(CO)_2$(COMe) [d]	2018, 1963	[33]
$CpFe(CO)_2$Me [f]	2010, 1955	[34]
CpFe(CO)(PMe_3)(COMe) [e]	1878	[35]
CpFe(CO)(PMe_3)Me [b]	1910	[26]
$Cp^*Fe(CO)_2$(COMe) [g]	2003, 1945	[36]
$Cp^*Fe(CO)_2$Me	2040, 1985	[37]
Cp*Fe(CO)(PMe_3)(COMe) [h]	1891	[38]
Cp*Fe(CO)(PMe_3)Me [g]	1910	[27]
(C_5Ph_5)Fe(CO)(PMe_3)(COEt) [h]	1903	[23]
(C_5Ph_5)Fe(CO)(PMe_3)Et [h]	1893	[23]

[a] In cyclohexane.
[b] In *n*-hexane.
[c] In toluene.
[d] in Nujol.
[e] In KBr discs.
[f] In CS_2.
[g] In pentane.
[h] In CH_2Cl_2.

tadienyl ligands, listed in Table 2 [32], indicates that an increase of the electron density at the iron center (COMe vs. Me, CO vs. PMe_3, Tp vs. Tp^{iPr2}) induces a shift of the terminal CO vibrational frequencies to lower wavenumbers, caused by enhanced π-back donation to the CO ligands. The tendency is however less clear-cut in the Tp versus Cp, C_5Ph_5 and Cp* series. Nevertheless, the data suggest that the relative electron-donating ability of the facial ligands is Cp, Cp*, $C_5Ph_5 > Tp$. This trend is opposite to that reported for sandwich-type complexes, where electrochemical studies showed that the Tp ligand is more donating than the Cp ligand [25], but agrees with other Group 8 and 9 metal half-sandwich complexes that exhibit the general trend $Cp^* > Cp$, $Tp^* > Tp$ [4]. This comparison involves compounds of different coordination geometries and thus caution must be excerted when this tool is used to order the relative donor strength of the four ligands. The only thorough electrochemical and infrared examination of the relative electron-donating abilities of the two classes of ligands, reported by Tilset and Skagestad, demonstrated that the hydridotris(pyrazolyl)borate ligand is more electron donating than the cyclopentadienyl ligand ($Tp^* > Tp > Cp$) toward Cr, Mo, and W in Group 6 metal carbonyl complexes of the type $[(FL)M(CO)_3]^-$ (FL = Cp, Tp, Tp*) [6e].

3. Conclusion

We have presented a one-step synthesis of the acetyl iron complex $TpFe(CO)(PMe_3)(COMe)$ (**1**), starting from *cis*,*trans*-$Fe(CO)_2(PMe_3)_2MeI$ and using the potassium, rather than the previously reported sodium, salt of the hydrotris(pyrazolyl)borate anion. This reaction has been shown to be specific to the parent Tp ligand. The photodecarbonylation leads to the first octahedral methyl–iron complex featuring the hydrotris(pyrazolyl)borate ligand system. The product $TpFe(CO)(PMe_3)Me$ (**2**) has been characterized by an X-ray diffraction analysis. These complexes have electronic properties that are distinct from related CpFe, Cp*Fe and $(C_5Ph_5)Fe$ counterparts. This is apparent from the CO stretching frequencies comparison of analogous iron carbonyl complexes. It is noteworthy that compounds **1** and **2** represent the first TpFe analogues of the chiral piano-stool acyl and alkyl iron complexes $Cp^{\#}Fe(CO)(PR_3)R'$ ($Cp^{\#} = C_5H_5$, C_5Ph_5 or C_5Me_5; $PR_3 = PMe_3$, PPh_3; R′ = σ-bonded carbon ligand). Moreover, $TpFe(CO)(PMe_3)Me$ is a diamagnetic counterpart of complex $TpRe(CO)(PMe_3)(OSO_2CF_3)$, used as source of the chiral auxillary $[TpRe(CO)(PMe_3)]^+$ [39].

4. Experimental

All manipulations were carried out under an atmosphere of argon using Schlenk or vacuum-line techniques. Reagent grade toluene, pentane and hexane were predried and then distilled under argon from sodium benzophenone ketyl prior to use. Acetonitrile and dichloromethane were distilled under argon from P_2O_5. All glassware was oven-dried prior to use. Infrared spectra were obtained using a Bruker IFS28 FT-IR spectrometer (4000–400 cm^{-1}). The spectra were obtained as Nujol mulls between KBr disks or with a 1.0 mm path-length NaCl cavity cell. All the NMR spectra were acquired at 297 K on a multinuclear Bruker DPX 200 instrument. Chemical shifts are given in parts per million (ppm) relative to tetramethylsilane (TMS) for ^1H and ^{13}C-NMR spectra, and relative to external 85% H_3PO_4 for ^{31}P-NMR spectra. Cyclic voltammograms were recorded using a EG&G-PAR model 263 potentiostat/galvanostat. The working electrode was Pt disk electrode ($d = 0.4$ or 1.0 mm), the counter electrode was a Pt wire, and the saturated calomel electrode (SCE) or a Ag/Ag^+(MeCN) electrode were used as reference electrodes. Dichloromethane and acetonitrile solutions were 1.0 mM in the compound under study and 0.1 M in the supporting electrolyte n-$Bu_4N^+PF_6^-$. The $Cp_2Fe^{0/+}$ couple was used as an internal reference for the potential measurements. Elemental analyses were carried out at the Center for Microanalyses of the CNRS at Vernaison, France. KTp [40], KTp* [41], tBuTp^RLi (R = H, iPr, Ph) [22] and *cis*,*trans*-$Fe(CO)_2(PMe_3)_2MeI$ [18] were prepared according to published procedures, and other chemicals were purchased from commercial sources and used as received.

4.1. Preparation of $TpFe(PMe_3)(CO)(COMe)$ (1)

Complex *cis*,*trans*-$Fe(CO)_2(PMe_3)_2MeI$ (400 mg, 1.00 mmol) was dissolved in CH_2Cl_2 (30 ml), and solid $K[HB(pz)_3]$ (328 mg, 1.00 mmol) was added. The resulting suspension was stirred for 12 h, during which time the solution became orange. The solid (KI) was collected on a glass sintered frit and washed with CH_2Cl_2 (2 × 5 ml). The solution was dried in vacuo and the residue was extracted with n-hexane (3 × 5 ml). The extracts were combined, concentrated slightly, and cooled to −18 °C for 3 days to afford orange microcrystals of **1**. Yield: 326 mg (0.78 mmol, 78%). ^1H-NMR (200 MHz, $CDCl_3$) δ 7.88 (d, 1H, H-3, $^3J_{HH} = 2.2$ Hz), 7.84 (d, 1H, H-3′, $^3J_{HH} = 2.0$ Hz), 7.69 (d, 1H, H-3″, $^3J_{HH} = 2.2$ Hz), 7.65 (m, 3H, H-5, H-5′, H-5″), 6.37 (t, 1H, H-4, $^3J_{HH} = 2.2$ Hz), 6.19 (t, 1H, H-4′, $^3J_{HH} = 2.0$ Hz), 6.15 (t, 1H, H-4″, $^3J_{HH} = 2.0$ Hz), 2.14 (s, 3H, $COCH_3$), 1.25 (d, 9H, $P(CH_3)_3$, $^2J_{HP} = 8.8$ Hz). $^{31}P\{^1H\}$ (81 MHz, CD_2Cl_2) δ 28.37 (s, PMe_3). IR (toluene, cm^{-1}): 1943 (s, ν(CO), 1586 (m, ν(COMe)).

4.2. *Preparation of TpFe(PMe$_3$)(CO)Me (**2**)*

A solution of TpFe(PMe$_3$)(CO)(COMe) (82 mg, 0.2 mmol) in toluene (50 ml) in a Pyrex bulb was photolyzed using an Hanovia 450 W high-pressure mercury vapor lamp. The lamp was jacketed by water, and the reaction bulb was placed ~2 cm away from the lamp. The whole system was wrapped with an aluminum foil. The orange solution was vigorously stirred and irradiated. The reaction was monitored by IR spectroscopy and was complete after 1 h. The solvent was evaporated under vacuum, and the residue was crystallized from hexane at −18 °C to give orange microcrystals of **2**. Yield: 62 mg (0.15 mmol, 80%). Anal. Calc. for $C_{14}H_{22}BFeN_6OP$: C, 43.34; H, 5.72; N, 21.66. Found: C, 43.59; H, 5.71; N, 21.35%. ^{1}H-NMR (200 MHz, CD_2Cl_2) δ 8.01 (d, 1H, H-3, $^3J_{HH} = 2$ Hz), 7.90 (d, 1H, H-3′, $^3J_{HH} = 2$ Hz), 7.75 (m, 3H, H-5, H-5′, H-5″), 7.64 (d, 1H, H-3″, $^3J_{HH} = 2.2$ Hz), 6.41 (t, 1H, H-4, $^3J_{HH} = 2.1$ Hz), 6.23 (t, 1H, H-4′, $^3J_{HH} = 2.1$ Hz), 6.17 (t, 1H, H-4″, $^3J_{HH} = 2.0$ Hz), 1.19 (d, 9H, P(C*H*$_3$)$_3$), $^2J_{HP} = 8.0$ Hz), −0.29 (d, 3H, Fe–C*H*$_3$, $^3J_{HP} = 4.0$ Hz). ^{13}C{^{1}H} NMR (50 MHz, CD_2Cl_2) δ 223.2 (d, CO, $^2J_{CP} = 35$ Hz), 143.6 (s, C-3), 142.82 (s, C-3′), 142.78 (s, C-3″), 135.7 (s, C-5 and C-5′), 135.2 (s, C-5″), 105.8 (s, C-4), 105.6 (s, C-4′ and C-4″), 15.8 (d, P(*C*H$_3$)$_3$, $J_{CP} = 24$ Hz), −5.7 (d, Fe–*C*H$_3$, $^2J_{CP} = 21$ Hz). ^{31}P{^{1}H} NMR (81 MHz, CD_2Cl_2) δ 32.92 (s, PMe$_3$). IR (Nujol, cm^{-1}): 1912 (s, ν(CO)).

4.3. *Crystal structure determination of TpFe(CO)(PMe$_3$)Me (**2**)*

Orange plates of **2** were obtained by slow diffusion of pentane into a saturated solution of the complex in dichloromethane, under argon, at room temperature. Crystal data: $C_{14}H_{22}BFeN_6OP$, $M_r = 388.01$, orthorhombic, P_{bcn}, $a = 12.640(4)$ Å, $b = 15.533(9)$ Å, $c = 18.654(5)$ Å, $V = 3662(3)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.407$ g cm^{-3}, $\mu = 9.24$ cm^{-1}, empirical absorption correction applied, $F(000) = 1616$, $T = 293(2)$ K, 2θ max: 54°, reflections collected/unique/used: 3962/3962/2849 ($I > 2\sigma(I)$), parameters refined: 230, R/R_{w2} ($I > 2\sigma(I)$) = 0.048/0.141, R/R_{w2} (all data) = 0.0709/0.1513, GOF = 0.920, $[\Delta\rho]_{min}/[\Delta\rho]_{max}$: −0.775/0.517. A crystal of approximate dimensions 0.38 × 0.32 × 0.15 mm was cemented onto quartz fibers with epoxy glue, and measured on an automatic CAD4 NONIUS diffractometer, using graphite-monochromated Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å) [42]. The structure was solved by direct methods with the program SIR-97 [43] which revealed a static disorder between the methyl and the carbonyl groups. Structure refinement by least-squares methods based on F^2 was carried out using the program SHELXL-97 [44]. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in calculated positions and were refined riding with the atoms to which they were bonded. The ORTEP view of the molecule was generated with PLATON-98 [45].

5. Supplementary material

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Center as supplementary publication CCDC No. 198117. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] (a) S. Trofimenko, The Coordination Chemistry of Polypyrazolylborate Ligands, Imperial College Press, London, 1999;
(b) S. Trofimenko, Chem. Rev. 93 (1993) 943.

[2] Abbreviations: pz = $C_3H_3N_2^-$, Tp = HB(pz)$_3^-$, Tp^R = HB(3-Rpz)$_3^-$ according to the nomenclature for poly(pyrazolyl)borate ligands and their complexes proposed by S. Trofimenko in reference [1].

[3] The cone angles of the κ^3-hydrotris(pyrazolyl)borato ligand HB(PZ)$_3$ (Tp) is somewhat larger than 180°, well above the 100° calculated for the ν^5-C_5H_5 (Cp); see reference [6a].

[4] Pertinent data on the relative electron-donating abilities of Tp, Cp, and their methylated derivatives have been recently summarized: D.M. Tellers, S.J. Skoog, R.G. Bergman, T.B. Gunnoe, W.D. Harman, Organometallics 19 (2000) 2428.

[5] Nb: (a) M. Etienne, F. Biasotto, R. Mathieu, J.L. Templeton, Organometallics 15 (1996) 1106;
(b) M. Etienne, B. Donnadieu, R. Mathieu, J. Fernández Baeza, F. Jalón, A. Otero, M.E. Rodrigo-Blanco, Organometallics 15 (1996) 4597.

[6] Group 6 metals: (a) M.D. Curtis, K.-B. Shiu, W.M. Butler, J.C. Huffman, J. Am. Chem. Soc. 108 (1986) 3335;
(b) K.-B. Shiu, L.-Y. Lee, J. Organomet. Chem. 348 (1988) 357;
(c) J.K. Kochi, T.M. Bockman, Adv. Organomet. Chem. 23 (1991) 51;
(d) J.H. MacNeil, W.C. Watkins, M.C. Baird, K.F. Preston, Organometallics 11 (1992) 2761;
(e) V. Skagestad, M. Tilset, J. Am. Chem. Soc. 115 (1993) 5077;
(f) J.D. Protasiewicz, K.H. Theopold, J. Am. Chem. Soc. 115 (1993) 5559.

[7] Ru: (a) E. Ruba, W. Simanko, K. Mereiter, R. Schmid, K. Kirchner, Inorg. Chem. 39 (2000) 382;
(b) M.S. Sanford, L.M. Henling, R.H. Grubbs, Organometallics 17 (1998) 5384.

[8] Ir: (a) D.M. Tellers, R.G. Bergman, Organometallics 20 (2001) 4819;
(b) E. GutierrezPuebla, A. Monge, M. Paneque, M.L. Poveda, S. Taboada, M. Trujillo, E. Carmona, J. Am. Chem. Soc. 121 (1999) 346.

[9] See, for example: R.C. Kerber, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 7, Pergamon, Oxford, 1995; Chapter 2.

[10] F.A. Cotton, B.A. Frenz, A. Shaver, Inorg. Chim. Acta 7 (1973) 161.

[11] R.B. King, A. Bond, J. Am. Chem. Soc. 96 (1974) 1343.

[12] S. Anderson, A.F. Hill, A.J.P. White, D.J. Williams, Organometallics 17 (1998) 2665.

[13] G. Bellachioma, G. Cardaci, V. Gramlich, A. Macchioni, F. Pieroni, L.M. Venanzi, J. Chem. Soc. Dalton Trans. (1998) 947.

[14] (a) M. Akita, N. Shirasawa, S. Hikichi, Y. Moro-oka, Chem. Commun. (1998) 973;
(b) N. Shirasawa, M. Akita, S. Hikichi, Y. Moro-oka, Chem. Commun. (1999) 417;
(c) N. Shirasawa, T.T. Nguyet, S. Hikichi, Y. Moro-oka, M. Akita, Organometallics 20 (2001) 3582.

[15] R.B. King, A. Bond, J. Am. Chem. Soc. 96 (1974) 1334.

[16] S. Anderson, A.F. Hill, A.M.Z. Slawin, D.J. Williams, J. Chem. Soc. Chem. Commun. (1993) 266.

[17] M.I. Bruce, D.N. Sharrocks, F.G.A. Stone, J. Organomet. Chem. 31 (1971) 269.

[18] M. Pankowski, M. Bigorgne, J. Organomet. Chem. 30 (1971) 227.

[19] M. Akita, K. Ohta, Y. Takahashi, S. Hikichi, Y. Moro-oka, Organometallics 16 (1997) 4121.

[20] H.B. Gray, G.P. Haight, Basic Principles of Chemistry, W.A. Benjamin, Mauro Park, 1967.

[21] (a) A. Loupy, B. Tchoubar, D. Astruc, Chem. Rev. 92 (1992) 1141;
(b) D. Astruc, M.-H. Delville-Desbois, M. Lacoste, J. Ruiz, F. Moulines, J.-R. Hamon, in: N. Hosmane (Ed.), Recent Advances in the Chemistry of the Main-Group Elements. Phosphorus, Sulfur, Silicon and the Related Elements, 1994, p. 11.

[22] O. Graziani, Ph.D. thesis, Université de Rennes 1, 2001.

[23] P. Brégaint, J.-R. Hamon, C. Lapinte, Organometallics 11 (1992) 1417.

[24] J.P. Jesson, S. Trofimenko, D.R. Eaton, J. Am. Chem. Soc. 89 (1967) 3148.

[25] P.R. Sharp, A.J. Bard, Inorg. Chem. 22 (1983) 2689.

[26] H.G. Alt, M. Herberhold, M.D. Rausch, B.H. Edwards, Z. Naturforsch. 34B (1979) 1070.

[27] C. Lapinte, D. Catheline, D. Astruc, Organometallics 7 (1988) 1683.

[28] Sandwich-type complexes: (a) J.D. Oliver, D.F. Mullica, B.B. Hutchinson, W.O. Milligan, Inorg. Chem. 19 (1980) 165;
(b) Y. Sohrin, H. Kokusen, M. Matsui, Inorg. Chem. 34 (1995) 3928;
(c) S.J. Mason, C.M. Hill, V.J. Murphy, D. O'Hare, D.J. Watkin, J. Organomet. Chem. 485 (1995) 165.

[29] Half-sandwich-type complexes: (a) K. Kim, S.J. Lippard, J. Am. Chem. Soc. 118 (1996) 4914;
(b) M. Ito, H. Amagai, H. Fukui, N. Kitajima, Y. Moro-oka, Bull. Chem. Soc. Jpn. 69 (1996) 1937;
(c) T. Ogihara, M. Akita, Y. Moro-oka, Inorg. Chem. 37 (1998) 2614;
(d) N. Arulsamy, D.S. Bohle, B. Hansert, A.K. Powell, A.J. Thomson, S. Wocaldo, Inorg. Chem. 37 (1998) 746.

[30] (a) A.N. Chernega, A.J. Graham, M.L.H. Green, J. Haggitt, J. Lloyd, C.P. Mehnert, N. Metzler, J. Souter, J. Chem. Soc. Dalton Trans. (1997) 2293.;
(b) G. Poignant, S. Sinbandhit, L. Toupet, V. Guerchais, Angew. Chem. Int. Ed. Engl. 37 (1998) 963;
(c) L. Li, A. Decken, B.G. Sayer, M.J. McGlinchey, P. Brégaint, J.-Y. Thépot, L. Toupet, J.-R. Hamon, C. Lapinte, Organometallics 13 (1994) 682.

[31] R.H. Magnuson, S. Zulu, W.-M. T'sai, W.P. Giering, J. Am. Chem. Soc. 102 (1980) 6887.

[32] Considering the relatively small differences between the ν(CO) stretching frequencies and the fact that ν(CO) stretches are well known to be dependent on experimental conditions, caution must be excerted in comparing the IR data gathered in Table 2 which have been recorded under various conditions.

[33] R.B. King, J. Am. Chem. Soc. 85 (1963) 1918.

[34] R.B. King, Organomet. Synth. 1 (1965) 151.

[35] P.M. Treichel, D.A. Komar, J. Organomet. Chem. 206 (1981) 77.

[36] S. N'Late, Ph.D. thesis, Université de Rennes 1, 1993.

[37] D. Catheline, D. Astruc, J. Organomet. Chem. 226 (1982) C52.

[38] V. Mahias, S. Cron, L. Toupet, C. Lapinte, Organometallics 15 (1996) 5399.

[39] T.P. Gunnoe, M. Sabat, W.D. Harman, Organometallics 19 (2000) 728.

[40] S. Trofimenko, J. Am. Chem. Soc. 89 (1967) 3170.

[41] S. Trofimenko, J. Am. Chem. Soc. 89 (1967) 6288.

[42] C.K. Fair, MOLEN. An Interactive Intelligent System for Crystal Structure Analysis, ENRAF-NONIUS, Delft, The Netherlands, 1990.

[43] A. Altomare, M.C. Burla, M. Camalli, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagn, SIR97, a program for automatic solution of crystal structures by direct methods, J. Appl. Crystallogr. 32 (1999) 115.

[44] G.M. Sheldrick, SHELX97 A Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.

[45] A.L. Spek, PLATON-98. A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 1998.