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Carbonyl derivatives of iron(0) from the reaction of $FeR_2(bipy)_2$ (R = Me, Et) with carbon monoxide

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Abstract

The reaction of $FeR_2(bipy)_2$, R = Me, Et, with CO proceeds with reductive elimination of acetone or diethylketone and formation of carbonyl derivatives of iron(0). The nature of the carbonyl derivatives depends on the solvent, $Fe_2(bipy)_2(CO)_5$ and $Fe(bipy)(CO)_3$ being isolated in heptane and toluene, respectively. Conversion of $Fe_2(bipy)_2(CO)_5$ to $Fe(bipy)(CO)_3$ takes place in toluene under a CO atmosphere. The tricarbonyl derivative $Fe(bipy)(CO)_3$, alternatively prepared by reaction of $FeCl_3$ with Nabipy in DME under a CO atmosphere, was studied by X-ray diffraction methods.

Keywords: Iron; Bipyridyl; Structures; Carbonyl; Complexes

1. Introduction

The reaction of carbon monoxide with transition metal alkyls is well known since 1957, when the carbonylation of methyl- and phenylpentacarbonylmanganese(I), $MnR(CO)_5$, to the corresponding acetyl or benzoyl derivatives, $Mn(RCO)(CO)_5$, was discovered [1]. Since then, the insertion reaction of CO into a metal–alkyl bond has been studied extensively due to its importance in both academy and industry [2]. It has been observed that the nature of the metal atom strongly influences the insertion products: for example, formation of η^2-acyl derivatives is often observed [3], especially in the case of the highly oxophilic alkyl derivatives of early transition elements [3a,3b,3c,3d,3e,3f]. In many cases, the insertion product is unstable and undergoes reductive elimination [4].

As far as Group 8 metals are concerned, the reaction of carbon monoxide with metal–alkyls to give acyl- or aroyl derivatives is well known for compounds containing tertiary phosphine as ancillary ligands [5]. However, little is known on the carbonylation reaction of derivatives containing nitrogen ligands [6].

As far as iron alkyl compounds are concerned, some years ago Kochi and coworkers [7] reported that $FeR_2(bipy)_2$, bipy = 2,2′-bipyridyl, R = Me, Et, reacts with carbon monoxide in THF at ca. 0 °C to give the ketone R_2CO and the diketone RC(O)C(O)R, R = Me, Et, Pr^n. The fate of the iron-containing moiety was not established. In the framework of our studies concerning the iron(II) adducts of polydentate amines, we decided to investigate this system in detail in order to possibly identify the products formed in the reaction. In this article we show that $FeR_2(bipy)_2$, R = Me, Et, undergo carbonylation in hydrocarbon solvents to give acetone or diethylketone exclusively and different types of iron(0) carbonyl derivatives depending on the reaction conditions.

2. Results and discussion

First we decided to run the carbonylation in toluene rather than in THF, due to the fact that the dialkyl derivatives slowly decompose in the oxygenated solvent [8], vide infra. At room temperature, a suspension of $FeR_2(bipy)_2$, R = Me, Et, in toluene absorbs CO up to a CO–Fe molar ratio of 2.8 (R = Me) and 2.7 (R = Et). In

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both cases, the absorption is fast and becomes negligible after ca. 20 min; the IR spectrum of the resulting green solution shows absorptions at 1983, 1910 and 1718 cm^{-1}. The two absorptions at higher wavenumbers are due to the iron(0) dipy derivative $Fe(bipy)(CO)_3$ (vide infra), while the latter one was assigned to acetone or diethylketone (detected also by GC–MS analysis), formed according to Eq. (1).

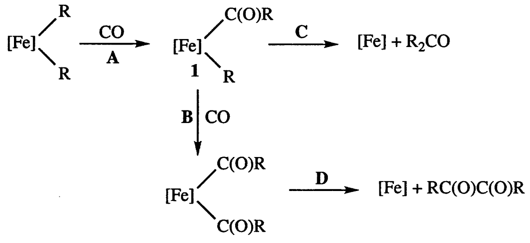
$$FeR_2(bipy)_2 + 4CO \rightarrow Fe(bipy)(CO)_3 + R_2CO + dipy \quad (1)$$

As the CO–Fe molar ratio is lower than 4 and some insoluble compound is formed during the reaction, the occurrence of some decomposition is likely to occur (uncoordinated dipy was present in the reaction mixture, see Section 4). In this connection, Yamamoto et al. found that $FeEt_2(bipy)_2$ decomposes in benzene solution at ca. 50 °C with loss of bipy and release of ethane and ethylene, the decomposition rate depending on the presence of polar solvents or π-acid species such as olefins [8].

Due to the fact that Kochi and coworkers obtained the ketone R_2CO and the diketone RC(O)C(O)R on carbonylating $FeR_2(bipy)_2$ at 0 °C in THF, and observed that the yield of diketone decreases on increasing the temperature (we have confirmed that RC(O)C(O)R is not formed in detectable amounts upon carbonylation in THF at 20 °C), we attempted a carbonylation experiment in toluene at ca. −50 °C. We observed no CO absorption until the temperature raised to ca. 10 °C: carbonylation at this temperature afforded the ketone. No diketone was observed.

The carbonyl compounds R_2CO and RC(O)C(O)R can be accounted by the usual mechanism involving the CO insertion into the M–R bond followed by reductive elimination of the carbonyl compound as depicted in Scheme 1. According to Scheme 1, the relative amounts of diketone and ketone are determined by the tendency of the monoacyl intermediate **1** to undergo reductive elimination (path **C**) or CO insertion (path **B**), a mechanism largely influenced by the temperature.

Carbonylations were also run in heptane. The reaction is much slower probably due to the low solubility of $FeR_2(bipy)_2$ in this medium but the final CO–Fe molar ratio (CO–Fe = 2.6 for R = Me) is similar to that obtained in toluene (CO–Fe = 2.8). Again, acetone or diethylketone are formed in 80 and 50% yield with respect to iron.



Scheme 1.

The reaction medium influences the iron-containing products, a problem which remained unsolved after the work of Kochi and coworkers. In toluene, partial evaporation of the solvent followed by addition of heptane afforded deep green crystals of $Fe(bipy)(CO)_3$ [9], whose synthesis was originally reported in 1982 by Frühauf and coworkers. We have found that the compound crystallizes as the bipy solvate $Fe(bipy)(CO)_3 \cdot 0.5bipy$ in the monoclinic space group $P2_1/n$. The $Fe(bipy)(CO)_3$ units are aligned along the crystallographic axis *a* with eclipsed amine ligands and staggered $Fe(CO)_3$ groups in order to minimize the steric repulsions. Similar overlap occurs within the lattice bipy molecules.

Iron is pentacoordinated to the nitrogen atoms of the bipy ligand and to the three carbon atoms of the carbonyl ligands in a slightly distorted trigonal pyramidal geometry, the axial position being occupied by N(1) and C(2), see Fig. 1. The entity of the distortion clearly appears from the value of the bond angles at iron: C(2)–Fe–N(1) = 174.97(15); N(1)–Fe–N(2) = 79.64(12); C(1)–Fe–N(1) = 93.87(15); C(3)–Fe–N(1) = 91.49(15)°. Table 1 lists a selection of bond distances and angles.

The bipy moiety occupies the axial–equatorial positions with Fe–N distances of 1.974(3) and 1.995(3) Å for the axial and the equatorial bonds, respectively. The observed axial–equatorial coordination of bipy is in agreement with spectroscopic studies [10] on carbonyl substitution reactions involving N-ligands.

Bond distances and angles within the iron-coordinated ligand are similar to those observed in the lattice or in the uncomplexed molecule [11], the main difference being the distance between the carbon atoms connecting the rings: C(8)–C(9) = 1.457(5) with respect to 1.490(3) Å [11]. Moreover, the lattice bipy has the nitrogen atoms on opposite sides as observed in the uncomplexed molecule. The rotation around the C–C bond on

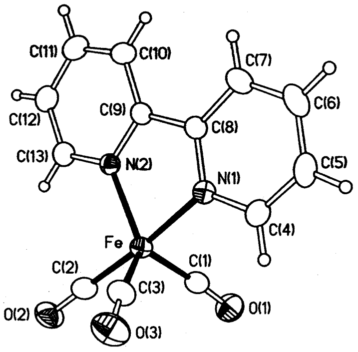


Fig. 1. View of the molecular structure of $Fe(bipy)(CO)_3 \cdot 0.5bipy$. Thermal ellipsoids are drawn at 30% probability level.

Table 1
Bond distances (Å) and angles (°) in $Fe(bipy)(CO)_3 \cdot 0.5bipy$

Bond distances			
Fe–C(2)	1.757(4)	Fe–C(1)	1.773(4)
Fe–C(3)	1.777(4)	Fe–N(1)	1.974(3)
Fe–N(2)	1.995(3)	C(1)–O(1)	1.152(5)
C(2)–O(2)	1.154(5)	C(3)–O(3)	1.152(5)
C(8)–C(9)	1.457(5)		
Bond angles			
C(2)–Fe–C(1)	89.94(18)	C(2)–Fe–C(3)	89.92(18)
C(1)–Fe–C(3)	114.33(18)	C(2)–Fe–N(1)	174.97(15)
C(1)–Fe–N(1)	93.87(15)	C(3)–Fe–N(1)	91.49(15)
C(2)–Fe–N(2)	95.62(15)	C(1)–Fe–N(2)	120.07(15)
C(3)–Fe–N(2)	125.26(16)	N(1)–Fe–N(2)	79.64(12)

Estimated standard deviations in parentheses refer to the least significant digit.

coordination is a well-known phenomenon in the field of complexes containing polypyridinic systems [12].

The geometrical parameters within the $Fe(CO)_3$ fragment [Fe–C (av.) = 1.767 Å; C–O (av.) = 1.156 Å] are in the range observed [Fe–C (av.) = 1.76–1.80 Å; C–O (av.) = 1.14–1.18 Å] in iron(0) carbonyl derivatives of general formula $Fe(NN)(CO)_3$, NN = bidentate nitrogen ligand [13].

To the best of our knowledge, the compound reported in this paper represents the fist example of a structurally characterized mononuclear dipy adduct of iron carbonyl, the only other bipy complexes of iron(0), $Fe_2(bipy)(CO)_7$ [14] and $Fe_2(bipy)(PBu^n_3)(CO)_6$ [15], being dinuclear.

Due to the fact that the preparations of $Fe(bipy)(CO)_3$ [9] reported so far require the preliminary synthesis of iron(0) carbonyl derivatives, we reckoned that a direct synthesis of the compound would have been of interest. As a matter of fact, we found that the reaction of a CO-saturated DME solution of Nabipy (as obtained from equimolar amounts of Na and bipy [16]) [17] with anhydrous $FeCl_3$ is slightly exothermic and readily absorbs CO, reaction (2). The IR spectrum

$$FeCl_3 \xrightarrow[DME]{Nabipy,\ CO} Fe(bipy)(CO)_3 \qquad (2)$$

of the deep green solution shows two strong absorptions at 1978 and 1903 cm^{-1}. Working up of the reaction mixture affords crystalline $Fe(bipy)(CO)_3$ in 70% yield. When the reaction was repeated in a gas volumetric apparatus, absorption of CO was observed up to a CO–Fe molar ratio of 2.2, presumably due to some parasitic reactions (vide infra).

The detailed investigation of the system has shown that $Fe(bipy)(CO)_3$ is stable in DME or in the presence of excess of bipy but is quickly decomposed by $FeCl_3$ with formation of $FeCl_2(bipy)$ [18], see Eq. (3a). It is noteworthy that the reaction reported in Eq. (3a) is reminescent of the preparation of $Fe_4Cl_8(THF)_6$ from $FeCl_3$ and Fe in THF [19], Eq. (3b). On assuming that the low solubility of $FeCl_2(bipy)$ in DME precludes its further carbonylation, we can rationalize the insufficient CO–Fe molar ratio observed in the reductive carbonylation of $FeCl_3$ as due to the parasitic reaction of $Fe(bipy)(CO)_3$ with the still unreacted $FeCl_3$. In this connection it is important to observe that $FeCl_2$ or $FeCl_2(bipy)_2$ undergo slow carbonylation in the presence of Na–bipy or Na in DME, respectively, the yields of $Fe(bipy)(CO)_3$ being rather poor (ca. 15%) even after prolonged reaction times.

$$Fe(bipy)(CO)_3 + 2FeCl_3 + 2bipy \rightarrow 3FeCl_2(bipy) + 3CO \qquad (3a)$$

$$4Fe + 8FeCl_3 + 18THF \rightarrow 3Fe_4Cl_8(THF)_6 \qquad (3b)$$

In consideration of the decrease of the Fe–X bond strength on increasing the atomic weight of the halide, we decided to test the carbonylation of $FeI_2(bipy)_2$ [8a] under reducing conditions. Surprisingly, $FeI_2(bipy)_2$ does not react with sodium–CO in DME even after prolonged periods of time. This suggests that the formation of the sodium halide and its solubility in the reaction medium is the driving force of the carbonylation reaction.

When the carbonylation of $FeR_2(bipy)_2$ was performed in heptane, a slower reaction was observed and a dark solid was isolated. An IR spectrum of the solution in the 2000–1600 cm^{-1} region showed one absorption only at 1718 (R = Me) or 1723 cm^{-1} (R = Et) attributed to the formation of R_2CO (R = Me, Et). An IR spectrum of the solid showed five absorptions between 1980 and 1700 cm^{-1} (1922m, 1889vs, 1855m, 1841m, 1701m-s cm^{-1} in toluene). This compound, slightly soluble in toluene, DME and THF and insoluble in aliphatic hydrocarbons, was identified as $Fe_2(bipy)_2(CO)_5$ from C, H, N and CO analysis. The iron(0) derivative reacts with CO in toluene with absorption of 1 mol of carbon monoxide to give $Fe(bipy)(CO)_3$, see Eq. (4), the low solubility of $Fe_2(bipy)_2(CO)_5$ in heptane being probably the reason of the incomplete carbonylation observed in such medium.

$$Fe_2(bipy)_2(CO)_5 + CO \rightarrow 2Fe(bipy)(CO)_3 \qquad (4)$$

3. Conclusions

This paper has proved that the organometallic products of the carbonylation of $FeR_2(bipy)_2$ depend on the reaction medium. Although the reaction is accompanied by some parasitic reactions due to the low thermal stability of the iron(II) dialkyls even in hydrocarbon solvents, we can state that iron(0) bipy carbonyl adducts are the reduction products of the carbonylation. As a matter of fact, $Fe_2(bipy)_2(CO)_5$, is formed in heptane while the mononuclear compound Fe(bipy)$(CO)_3$ is formed in toluene.

Moreover, we have shown that Fe(bipy)$(CO)_3$ is obtained in good yields by reductive carbonylation of $FeCl_3$ in DME at atmospheric pressure of CO.

4. Experimental

Unless otherwise stated, all of the operations were carried out under an atmosphere of prepurified Ar. Solvents were dried by conventional methods prior to use.

IR spectra were recorded on a FT-1725X instrument on solutions (0.1 mm CaF_2 windows) or Nujol or polychlorotrifluoroethylene (PCTFE) mulls prepared under rigorous exclusion of moisture and air.

The amounts of C_3H_6O or diethylketone were determined by IR spectroscopy measuring the area of the absorptions at 1718 (C_3H_6O in $C_6H_5CH_3$), 1723 (C_3H_6O in C_7H_{16}), 1718 (diethylketone in $C_6H_5CH_3$) and 1725 cm^{-1} (diethylketone in C_7H_{16}).

The following compounds were commercial products, used as received, or were prepared according to literature: $Fe(acac)_3$ [20], 2,2′-dipyridyl, bipy (Fluka), $FeCl_2\cdot 4H_2O$ (Aldrich), $FeCl_3$ [21], $AlEt_2OEt$ (Schering), $FeCl_2(bipy)_2$ [18a], $Fe(CO)_5$ (Merck), $Fe_2(CO)_9$ [22], $AlMe_3$ (2 M in C_6H_{14}, Aldrich), LiMe (1.6 M in Et_2O, Fluka). $FeCl_2$ was obtained by heating the hydrate $FeCl_2\cdot 6H_2O$ at 100 °C in vacuo for 72 h. Finely divided Na was obtained by suspending the commercial product (50% w/w suspension in paraffin, Aldrich) in $C_6H_5CH_3$ followed by filtration at ca. 50 °C, washing the solid with $C_6H_5CH_3$ and C_7H_{16} and drying in vacuo at room temperature (r.t.). The compound $FeI_2(bipy)_2$ was prepared according to a modification of the published procedure [8a]. A violet suspension of $FeEt_2(bipy)_2$ (0.794 g, 1.86 mmol) in $C_6H_5CH_3$ (25 ml) was treated dropwise at ca. 0 °C with a solution of I_2 (0.473 g, 1.86 mmol) in $C_6H_5CH_3$ (25 ml). After 12 h stirring at r.t., the solid was filtered off, washed with $C_6H_5CH_3$ (3 × 15 ml) and dried in vacuo at r.t. affording 0.901 g (78%) of $FeI_2(bipy)_2$ as a bright red microcrystalline solid. IR (Nujol, cm^{-1}): 3058w, 1602m, 1575w, 1561w, 1465s, 1441s, 1315m-w, 1245w, 1157m, 1062w, 1016m, 766s, 733m-s, 651w. Anal. Found: C, 38.5; H, 2.7; N, 8.7. Calc. for $C_{20}H_{16}FeI_2N_4$: C, 38.7; H, 2.6; N, 9.0%. The use of excess iodine afforded solids containing a I–Fe molar ratio higher than two.

4.1. *Preparation of $FeMe_2(bipy)_2$*

The method available in the literature [7] have been modified as follows.

4.1.1. *From $FeCl_2(bipy)_2$ and LiMe*

A dark blue suspension of $FeCl_2(bipy)_2$ (1.523 g, 3.47 mmol) in $C_6H_5CH_3$ (40 ml) was cooled at ca. −78 °C and treated dropwise with a 1.6 M solution of LiMe in Et_2O (4.4 ml, 7.04 mmol of LiMe). The suspension turned violet while rising to r.t. After filtration, the volume of the solution was reduced to ca. 20 ml. After addition of C_7H_{16} (30 ml) the mixture was cooled overnight at ca. −30 °C. The cold suspension was filtered and the solid was dried in vacuo at r.t. affording 0.701 g (51% yield) of $FeMe_2(bipy)_2$ which was identified by spectroscopic (IR and NMR) and analytical methods and stored at ca. −30 °C in order to prevent its slow thermal decomposition.

4.1.2. *From $Fe(acac)_3$ and $AlMe_2(OMe)$*

A red–orange mixture of $Fe(acac)_3$ (4.54 g, 12.9 mmol) and bipy (4.74 g, 30.3 mmol) in Et_2O (40 ml) was treated dropwise at ca. −20 °C with a solution of $AlMe_2(OMe)$ [from the 1:1 reaction of $AlMe_3$ (37.0 mmol) with the equimolar amount of MeOH in C_6H_{14}]. The mixture was allowed to warm up to r.t. and after 12 h stirring at r.t., a blue–black solid was present. The suspension was diluted with Et_2O (50 ml) and the solid was filtered off, washed with Et_2O (6 × 10 ml), C_7H_{16} (3 × 10 ml) and dried in vacuo affording $FeMe_2(bipy)_2$ (93% yield) which was identified by spectroscopic (IR and NMR) and analytical methods and stored at ca. −30 °C.

4.2. *Preparation of $FeEt_2(bipy)_2$*

The methods available in the literature [8] has been modified as follows. A red–orange mixture of $Fe(acac)_3$ (4.56 g, 12.9 mmol) and bipy (4.74 g, 30.3 mmol) in Et_2O (25 ml) was treated dropwise at ca. −20 °C with $AlEt_2(OEt)$ (5.5 ml, 36.7 mmol). The mixture was allowed to warm up to r.t. and after 12 h of stirring at r.t., a blue–black solid was present. The solid was filtered off, washed with Et_2O (5 × 10 ml), C_7H_{16} (3 × 10 ml) and dried in vacuo affording $FeEt_2(bipy)_2$ (55% yield) which was identified by spectroscopic (IR and NMR) and analytical methods and stored at ca. −30 °C.

4.3. *Carbonylation of $FeR_2(bipy)_2$ ($R = Me$, Et)*

4.3.1. *In $C_6H_5CH_3$*

A violet suspension of $FeMe_2(bipy)_2$ (0.687 g, 1.72 mmol) in $C_6H_5CH_3$ (50 ml) was treated with CO at 1 atm total pressure and 20 °C. The mixture turned green. After 16 h stirring at r.t., an IR spectrum of the solution revealed strong absorptions at 1983 and 1910 cm^{-1} and a band of lower intensity at 1718 cm^{-1}. The suspension was filtered, the volume of the solution was reduced to ca. 25 ml and C_7H_{16} (30 ml) was added. The mixture was cooled overnight at ca. −30 °C and filtered at low temperature to give Fe(bipy)$(CO)_3$ [23] as a black–green crystalline solid (0.322 g, 63% yield), identified by spectroscopic (IR and NMR) and analytical methods.

By operating in a similar way, Fe(bipy)$(CO)_3$ was obtained (67% yield) from the carbonylation reaction of $FeEt_2(bipy)_2$.

A gas volumetric control of the carbonylation reaction showed that $FeR_2(bipy)_2$ in $C_6H_5CH_3$ absorbed CO at 23.6 °C up to a CO–Fe molar ratio of 2.8 (R = Me) or 2.7 (R = Et) in a 3 h time. The CO–Fe molar ratio after 17 h was 3.0 in the case of $FeMe_2(bipy)_2$ and substantially unchanged in the case of the ethyl derivative. A GC–MS analysis of the solutions coupled with a quantitative determination by IR spectroscopy showed the formation of C_3H_6O (C_3H_6O–Fe molar ratio = 0.53) or diethylketone (diethylketone–Fe molar ratio = 0.40). A GC–MS of the volatiles, collected in a cold (−196 °C) trap while heating the solutions at ca. 30 °C in vacuo, revealed the presence of dipy, C_3H_6O or diethylketone.

When the carbonylation of $FeMe_2(bipy)_2$ was repeated at ca. −50 °C, the other experimental conditions being substantially the same, no reaction was observed until the temperature raised to ca. 10 °C. An IR spectrum of the solution after carbonylation had strong absorptions at 1983 and 1910 cm^{-1} and a band of lower intensity at 1718 cm^{-1}. A GC–MS analysis of the solutions coupled with a quantitative determination by IR spectroscopy showed the formation of C_3H_6O (C_3H_6O–Fe molar ratio = 0.52).

An IR spectrum recorded a short time (5 min) after the admission of CO into a suspension of $FeMe_2(bipy)_2$ in $C_6H_5CH_3$ showed the same absorptions at 1982 and 1911 and 1719 cm^{-1}, increasing with time.

4.3.2. In C_7H_{16}

The experimental details are reported for $FeMe_2(bipy)_2$, the reaction being performed in a similar way for the ethyl compound. A suspension of $FeMe_2(bipy)_2$ (0.366 g, 0.92 mmol) in C_7H_{16} (25 ml) was treated with CO at atmospheric pressure. Absorption of CO was observed. After 15 h stirring at r.t., an IR spectrum of the almost colourless solution showed one absorption only at 1717 cm^{-1}. Acetone was detected (C_3H_6O–Fe molar ratio = 0.8) by GC–MS and IR analysis. The solid was filtered, washed with C_7H_{16} and dried in vacuo at r.t. affording $Fe_2(bipy)_2(CO)_5$ (0.241 g, 93% yield) as an air sensitive black solid, slightly soluble in $C_6H_5CH_3$ or DME. Anal. Found: C, 52.9; H, 3.1; CO (decomposition of the sample with a concd. Py solution of I_2), 24.2; N, 10.3. Calc. for $C_{25}H_{16}Fe_2N_4O_5$: C, 53.2; H, 2.9; CO, 24.8; N, 9.9%. IR (Nujol, cm^{-1}): 3063w, 1923m-w, 1890vs, 1855m-w, 1842m-w, 1702m-s, 1600m, 1515m-w, 1260m-s, 1170w, 1009m, 759m-s, 642m. IR ($C_6H_5CH_3$, cm^{-1}): 1922m-w, 1889vs, 1855m, 1841m, 1701m-s. IR (DME, cm^{-1}): 1920m-w, 1893vs, 1855m, 1841m, 1701m-s. The carbonylation of $FeEt_2(bipy)_2$ afforded the same iron carbonyl compound and diethylketone (ketone–Fe molar ratio = 0.5).

A gas volumetric control of the carbonylation reaction showed that $FeMe_2(bipy)_2$ in C_7H_{16} absorbed CO at 23.6 °C up to a CO–Fe molar ratio of 2.6 in a 12 h time.

4.4. Syntheses of Fe(bipy)$(CO)_3$

A solution of bipy (4.0 g, 25.6 mmol) in DME (100 ml) were added of finely divided Na (0.589 g, 25.6 mmol) obtaining a deep violet solution. After stirring overnight at r.t., the solution was saturated with CO and solid $FeCl_3$ (1.392 g, 8.6 mmol) was added. An exothermic reaction with formation of a deep green suspension took place. The mixture was stirred under CO for 20 h, filtered and the solid was washed with DME until the washings were colourless (3 × 5 ml). The volume of the deep green solution was reduced to ca. 25 ml and $C_6H_5CH_3$ (25 ml) was added. The solid was filtered off and dried in vacuo at r.t. affording Fe(bipy)$(CO)_3$ (1.77 g, 70% yield). IR (Nujol, cm^{-1}): 3064w, 1972s, 1895w, 1869vs, 1582m-w, 1467m-s, 1458m-s, 1325w, 1310w, 1259m-s, 1165m-w, 758s, 634m-s, 613m-s, 583m-s, 450m-s. IR ($C_6H_5CH_3$, cm^{-1}): 1983s, 1910vs. IR (DME, cm^{-1}): 1978s, 1903vs.

A gas volumetric control of the carbonylation reaction showed that $FeCl_3$ in DME in the presence of Nabipy absorbed CO at 24.1 °C up to a CO–Fe molar ratio of 2.2 in a 12 h time.

The tricarbonyl derivative was obtained also from $FeCl_2$ or $FeCl_2(bipy)_2$ in low yields (15% yield in both cases), after 72 h stirring at r.t. No reaction was observed between $FeI_2(bipy)_2$ and Na in the presence of CO.

4.5. Fe(bipy)$(CO)_3$·0.5bipy. Crystal structure solution and refinement

Crystals of Fe(bipy)$(CO)_3$·0.5bipy were obtained from $C_6H_5CH_3$–C_7H_{16} mixture. Crystallographic data and details of the structure refinement for Fe(bipy)$(CO)_3$·0.5bipy are in Table 2. A dark–green prism of dimensions 0.60 × 0.28 × 0.26 mm was sealed in a glass capillary and mounted on a Bruker AXS P4 diffractometer equipped with graphite-monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å). The cell parameters, calculated from the setting angles of 36 reflections having $5.35 \leq \theta \leq 12.40°$, are listed in Table 2 together with some structural details. A total of 4723 intensity data between $2.6 \leq \theta \leq 27.0°$ was collected with the ω–2θ scan mode. Three standard reflections were mea-

Table 2
Crystallographic data and details of the structure refinement for Fe(bipy)$(CO)_3$ 0.5bipy

Chemical formula	Fe(bipy)$(CO)_3 \cdot$0.5bipy
Empirical formula	$C_{18}H_{12}FeN_3O_3$
Formula weight	374.16
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$ (No. 14)
Unit cell dimensions	
a (Å)	7.298(1)
b (Å)	14.231(1)
c (Å)	15.908(2)
β (°)	102.02(1)
V (Å^3)	1616.0(3)
Z	4
ρ_{calc} (mg m^{-3})	1.538
μ (mm^{-1})	0.956
F(000)	764
Θ Range for data collection (°)	2.62–27.00
Index ranges	$-9 \leq h \leq 1$, $-18 \leq k \leq 1$, $-20 \leq l \leq 20$
Reflections collected	4723
Independent reflections	3537 [$R_{int} = 0.0188$]
Completeness to $\Theta = 27.00°$	100.0%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3537/0/221
$R(F_o)$ [$I > 2\sigma(I)$]	0.045
$R_w(F_o^2)$ indices (all data)	0.0892
Goodness-of-fit on F^2	1.047

sured every 97 measurements to check sample decay and equipment stability. The intensities were corrected for Lorentz, polarization and absorption effects (ψ-scan method) [24]. After merging of equivalent reflections, 3537 independent reflections were obtained [R_{int}, $\Sigma |F_o^2 - F_{o\ (mean)}^2| / \Sigma [F_o^2] = 0.0188$].

The structure solution was obtained in the space group $P2_1/n$ by the standard Patterson and Fourier methods. The programme SHELX-97 was used for the refinement of the structure, based on full-matrix least-squares on F^2 [25]. The hydrogen atoms were located in the difference Fourier map, but were refined with the riding constraints. The final refinement cycles gave the reliability factors listed in Table 2.

4.6. Reaction of Fe(bipy)$(CO)_3$ with $FeCl_3$

A solution of Fe(bipy)$(CO)_3$ (0.343 g, 1.16 mmol) and bipy (0.363 g, 2.32 mmol) in DME (50 ml) was treated with $FeCl_3$ (0.215 g, 1.32 mmol). Immediate gas evolution was observed with formation of a red solid. An IR spectrum of the solution in the carbonyl stretching region showed absorptions at 1978 and 1903 cm^{-1} typical of Fe(bipy)$(CO)_3$. Addition of another equivalent of $FeCl_3$ (0.173 g, 1.07 mmol) caused further gas evolution and formation of a colourless suspension. The surnatant solution was found (IR) to be free from carbonyl compounds. The solid was filtered, washed with DME and dried in vacuo at r.t. affording 0.93 g (90% yield) of $FeCl_2$(bipy) [18a] identified by IR and analytical data.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 188666 for compound Fe(bipy)$(CO)_3 \cdot$0.5bipy. Copies of these data 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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