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Cyanide as a versatile Lewis base ligand at a dinitrogen-binding iron(II) centre: mono- and heteronuclear adducts

Sílvia S.P.R. Almeida^a, M. Fátima C. Guedes da Silva^{a,b}, Lucjan B. Jerzykiewicz^c, Piotr Sobota^c, Armando J.L. Pombeiro^{a,*}

^a Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Av. Rovisco pais, 1049-001 Lisbon, Portugal ^b Universidade Lusófona de Humanidades e Tecnologias, Campo Grande, 376, 1749-024 Lisbon, Portugal ^c Faculty of Chemistry, University of Wroclaw, 50-383 Wroclaw, Poland

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Dedicated to Professor João J.R. Fraústo da Silva in recognition of his achievements.

Abstract

The ligated cyanide in *trans*-[FeH(CN)(dppe)₂] is activated towards aroylation, alkylation and addition of various transition metal Lewis acids, in particular [WCl₄(PPh₃)₂], [ReOCl₃(PPh₃)₂], [PdCl₂(PPh₃)₂] and [PtCl(Ph)(PPh₃)₂], to give, in the former case, mononuclear isocyanide complexes and, in the latter case, heteronuclear adducts with bridging cyanide. Their syntheses and spectroscopic characterisation are presented, as well as results of the X-ray diffraction analyses of a trinuclear complex with the $\{Fe - C \equiv N - W - N \equiv C - Fe\}$ unit and of the parent cyano *trans*-[FeH(CN)(dppe)₂] complex. The cyanide bridge allows the electronic communication between the metal centres as indicated by a cyclic voltammetric study. \bigcirc 2003 Elsevier Science B.V. All rights reserved.

Keywords: Cyanide; Bridging cyanide; Isocyanide; Transition metal Lewis acid; Heteronuclear complexes

1. Introduction

The coordination chemistry of cyanide is a matter of widespread interest in various fields of chemistry and biochemistry, its origins remitting to about three centuries ago since the discovery of Prussian Blue, possibly the oldest known coordination compound.

A number of binding modes of cyanide are known (the most common being the terminal C-bound and the terminal C,N-bridging ones), conferring a high synthetic versatility to this ligand namely for the preparation of a wide variety of types of complexes [1] with relevance, e.g. in organometallic and inorganic chemistries, material and medicinal sciences. Cyano-bridged mixed valence complexes are within those which are attracting a high current interest in view of their potential use, e.g. in molecular electronics, molecular magnetism and electrochromism.

From a biological point of view, it is noteworthy to mention that aqueous cyanide is a known substrate of nitrogenase [2] and iron-cyanide complexes have been recognised in active sites of iron-only and iron-nickel hydrogenases [3].

Within our continuous interest on the investigation of the activation, by dinitrogen-binding metal sites, of nitrogenase substrates, such as nitriles [4–8], cyanamides [9–12], isocyanides [13–24], alkynes and alkynederived species [21–32], we have also been studying cyanide in particular at some Re^I [16,33–36] or Fe^{II} [17] phosphinic centres and its activation towards electrophiles. Hence, reaction of [NBu₄][*trans*-Re(CN)₂(dppe)₂] with a protic acid (HBF₄, [Et₃NH][BPh₄], CH₃COOH), added in stoichiometric amount, gives, on protonation of one of the cyano-ligands, the hydrogen isocyanide

^{*} Corresponding author. Tel.: +351-2184 19237; fax: +351-2184 64455/7.

E-mail address: pombeiro@ist.utl.pt (A.J.L. Pombeiro).

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complex *trans*-[Re(CN)(CNH)(dppe)₂], whereas the Hbonded cyano-adducts *trans*-[Re(CN·HOOCCF₃)₂-(dppe)₂], *trans*-[Re(CN·HOMe)₂(dppe)₂] and *trans*-[Re(CN·HNEt₃)(dppe)₂][BPh₄] are formed on reaction of the isocyanide complex *trans*-[Re(CN)(CNH)(dppe)₂] with an excess of CF₃COOH or of the parent dicyanocomplex with an excess of MeOH or [Et₃NH][BPh₄] [33] (Scheme 1(a, b)).

Protonation of a cyano-intermediate is believed to occur in the formation of the isocyanide complexes trans-[ReCl(CNH)(dppe)₂] and trans-[FeH(CNH)- $(dppe)_2$ ⁺ on reaction of *trans*-[ReCl(CNSiMe₃)(dppe)₂] with MeOH or HCl [16,36] or of *trans*-[FeHCl(dppe)₂] with NCSiMe₃ in the presence of $Tl[BF_4]$ and HBF_4 [17]. The isocyanide complex *trans*- $[FeH(CNH)(dppe)_2]^+$ can also be obtained by protonation (by HBF₄) of the cvano-complex trans-[FeH(CN)(dppe)₂] which can also add BPh₃ (Scheme 1c) to give the isocyanotriphenylborate product trans-[FeH(CNBPh₃)(dppe)₂] [17]. At the above Re^I centre, CNH can undergo further protonation to give the aminocarbyne complex trans-[Re- $Cl(CNH_2)(dppe)_2$ [16,18] and the { CNH_x } (x = 0, 1, 2) ligated species can be postulated [14,15,22,37] as sequential stages in the enzymatic reduction of cyanide. Such reactions have been recently reviewed [14,15].

We have now extended the study of the cyanocomplex *trans*-[FeH(CN)(dppe)₂] (whose crystal structure is also included) with the same binding metal centre as the related dinitrogen complex *trans*-[FeH(N₂)-(dppe)₂]⁺ [38], to other electrophilic agents and found that the ligated cyanide can readily undergo aroylation, alkylation and addition of various transition metal Lewis acids giving, in the latter case, di- or trinuclear adducts with bridging cyanide which can allow the interaction between the metal centres.

These studies, involving a nitrogenase substrate at a N_2 -binding metal site, appear particularly timely to celebrate the retirement of Professor Fraústo da Silva who, in 1971 (and following his overall and remarkable planning to bring expertise to the research Centre he was creating at the Instituto Superior Técnico) introduced one of us (A.J.L.P., then initiating his post-graduate training) in the area of Nitrogen Fixation.

2. Results and discussion

Treatment of a CH₂Cl₂ or THF solution of trans-[FeH(CN)(dppe)₂] with the appropriate aroylating or alkylating agent (RX = PhCOCl, MeI or $[Et_3O][BF_4]$, added in a stoichiometric amount or in a slight, ca. 3:1, molar excess) results in the electrophilic addition to the cyano-ligand to afford the corresponding isocyanide complex *trans*-[FeH(CNR)(dppe)₂]X [R = PhCO, X = Cl (1); R = Me, X = I (2); R = Et, $X = BF_4$ (3)] (Scheme 2). The reactions proceed smoothly at room temperature, leading to the products in isolated yields up to 60%. Compound 1 is new and, to our knowledge, provides the first example of an aroylation reaction of the ligating cyanide at the parent hydride-cyanide complex. The susceptibility of the CN⁻ ligand in this complex to alkylation to afford isocyanide complexes was first briefly reported by us [39], for instance in the preparation of 3 by using MeI as the alkylating agent, and later by others [40] using the organoiodide as the reaction solvent. The alkylation reaction also occurs [40] for other organo-iodides and -bromides as solvents. Our method does not require the use of the organo-halide as the solvent, the reaction proceeding in a more convenient and common organic solvent like CH₂Cl₂ or THF.

The related compounds *trans*-[FeH(CNMe)(dppe)₂]X (X = BF₄ or PF₆), with different counter-ions, were prepared by our group by treating a THF solution of *trans*-[FeHCl(dppe)₂] with methyl isocyanide (CNMe) in the presence of Tl[BF₄] [41,42] or Tl[PF₆] [42]. An identical procedure was followed [41,42] for the synthesis of **3** by using ethylisocyanide.

The electrophilic addition route towards the isocyanide complexes described in the present work, which involves the generation in situ of the CNR ligand, is more convenient and versatile than that involving free isocyanide as the starting reagent, because it does not require the synthesis and handling of the nasty, smelly and commonly unstable CNR compounds.

Furthermore, the nucleophilic character of the cyanoligand in *trans*-[FeH(CN)(dppe)₂] can be applied to the syntheses of di- and tri-nuclear adducts by following an electrophilic addition route similar to that described above, but using a transition metal Lewis acid as the electrophile. Hence, the dinuclear complex with a bridging cyanide [HFe(dppe)₂(μ -CN)PdCl₂(PPh₃)] (4) is obtained (Scheme 3) on reaction of *trans*-[FeH(CN)(dppe)₂] with [PdCl₂(PPh₃)₂] (used in stoichio-









metric amount), whereas the trinuclear [{HFe(dppe)₂(μ -CN)}₂(ReOCl₃)] (5) and [{HFe(dppe)₂(μ -CN)}₂-PtCl(Ph)] (6) are formed (Scheme 3) when using [ReOCl₃(PPh₃)₂] or [PtCl(Ph)(PPh₃)₂] (in ca. 0.5:1 molar ratio, relatively to the cyano-complex), correspondingly, as the transition metal Lewis acid source. In addition, the trinuclear species, [{XFe(dppe)₂(μ -CN)}₂WCl₃(OH)] (7) (X = Cl or OH) was formed upon reaction of *trans*-[FeH(CN)(dppe)₂] with [WCl₄(PPh₃)₂].

The proposed formulations are based on IR, ¹H and ${}^{31}P{}^{1}H$ NMR spectroscopies, positive-ion FAB mass spectra, elemental analysis, cyclic voltammetry and, for one of them (7), X-ray diffraction data.

In the IR spectrum of the isocyanide complex **1**, the two strong bands observed at 1881 and 1838 cm⁻¹ are assigned to the coupled v(C=N)/v(C=O) vibrations of the benzoylisocyanide ligand, whereas for the di- and tri-nuclear adducts v(C=N) is detected in the 1988–2074 cm⁻¹ range.

In the ¹H NMR (CD₂Cl₂) spectra, the hydride resonance is the expected high-field quintet (²J_{HP} = 46–47 Hz) at δ from -7.45 to -14.55, due to coupling to the 4 equiv. P nuclei. In comparison with the parent iron-cyanide complex (δ -14.85) a substantial lower field shift is observed for the cationic mononuclear compound **1** (δ -7.45), as found [42] for the related arylisocyanide complexes *trans*-[FeH(CNR)(dppe)₂]⁺ (R = aryl) (δ -8.6 to -9.9). However, in the case of the neutral di- and trinuclear adducts (δ -13.1 and -14.6 for **5** and **6**, respectively), except for **7** which is paramagnetic, only a relatively small shift occurs. In the ${}^{31}P{}^{1}H{}$ NMR spectra, a singlet is observed at $\delta - 50.1$ to -59.3 relative to P(OMe)₃ due to the P atoms of the chelating diphosphine, indicating the *trans* geometry for the Fe metal centres in each complex. In addition, for complex 4 the two higher field PPh₃ resonances (with the expected 1:4 integration relatively to that of the P-dppe signal) can possibly be ascribed to the *cis* and *trans* geometries around the Pd atom.

Further evidence for the proposed formulations is provided by the positive-ion FAB MS spectra which show various expected metal containing fragments and by X-ray data for complex 7. Although the X-ray structural analysis for this compound (whose molecular



Fig. 1. Molecular structure of the trinuclear species [{XFe(dppe)₂(μ -CN)}₂WCl₃(OH)] (7) (X = Cl or OH). Crystal data: monoclinic, $P2_1/c$, a = 24.028(4), b = 18.860(4), c = 20.319(5) Å, $\beta = 101.09(5)^{\circ}$.

structure is shown in Fig. 1) could not be fully refined due to disorder, the collected data unambiguously prove the trinuclear character of the complex with two ironcyano {XFe(dppe)₂(CN)} units bound, via bridging cyanides, to a central tungsten atom. The precise nature of X (Cl, OH or O) could not be ascertained by X-rays, but the consideration of an oxide (either at the Fe or at the W metals) is not supported by IR since no band that could be ascribed to v(Fe=O) or v(W=O) was observed. In any case, the formation of 7 formally involves hydride abstraction from iron and metal centre hydrolysis, i.e. of the W centre if X = Cl or of both the W and the Fe ones if X = OH. In the former hypothesis (X =Cl), iron chlorination also occurs, the {WCl₄} site conceivably behaving as the halogenating agent to give the $\{WCl_3\}$ centre in 7.

The complex *trans*-[FeH(CN)(dppe)₂] has been characterised by X-ray diffraction analysis, although also of a low quality crystal. The molecular structure is shown in Fig. 2, selected bond distances and angles are given in Table 1, and crystal data in Table 2. It presents the expected octahedral-type geometry with the diphosphines in the equatorial sites, the hydride and the CN^- ligands being mutually *trans* in the apical positions.

The Fe-C=N moiety is essentially linear [Fe-C1N-N angle of 173.3(13)°], and the Fe-C1N and C1N-N distances, 1.903(13) and 1.164(17) Å, are similar to those reported for the iron(II) complexes [FeH(CNBPh_3)-(dppe)_2] [17] [1.914(3) and 1.163(4) Å], [FeH(CNR)-(dppe)_2]⁺ [R = Me [43], 1.851(5) and 1.154(6) Å; R = (CH_2)_3I [40], 1.845(6) and 1.161(8) Å]. Moreover, the Fe-P (average) distance in the complex of this study, 2.230(4) Å, is similar to that found in the above neutral



Fig. 2. Molecular structure of trans-[FeH(CN)(dppe)2].

Table 1

Selected bond distances (Å) and angles (°) for complex *trans*- $[FeH(CN)(dppe)_2]$, with e.s.d.s. in parentheses

Bond distances	
Fe-P1	2.227(4)
Fe-P2	2.227(4)
Fe-P3	2.222(4)
Fe-P4	2.240(4)
Fe-C1N	1.903(13)
Fe-H1	1.65(9)
N-C1N	1.164(17)
Bond angles	
P1-Fe-P2	85.2(2)
P1-Fe-P3	169.9(2)
P1-Fe-P4	93.4(2)
P2-Fe-P3	95.5(2)
P2-Fe-P4	168.8(2)
P3-Fe-P4	84.0(2)
Fe-C1N-N	173.3(13)
C1N-Fe-H1	176(3)

Table 2									
Crystal o	data	and	structure	refinement	for	trans-	[FeH(CN)	(dpr

Chemical formula	C ₅₃ H ₄₈ FeNP ₄
Formula weight	879.66
λ (Å)	0.71073
$T(\mathbf{K})$	100(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	10.665(4)
b (Å)	24.224(6)
c (Å)	16.951(4)
β (°)	100.80(10)
V (Å ³)	4302(3)
Ζ	4
$\mu ({\rm mm}^{-1})$	0.538
$D_{\rm calc} ({\rm g \ cm^{-3}})$	1.358
F(000)	1840
θ Range (°)	3.19-28.38
Number of reflections mea-	9066
Number of unique reflections	5553
<i>P</i> .	0.0051
Number of observed reflec-	2306
tions $[I > 2\sigma(I)]$	2300
Weighting scheme (w)	$w = 1/[\sigma^2(F^2) + (0.0116P)^2]$ where
weighting scheme (w)	$P = (F_2^2 + 2F_2^2)^{2/3}$
Final R_1 indices $[I > 2\sigma(I)]$	$R_1 = 0.0956, wR_2 = 0.1056$
Final R_1 indices (all data)	$R_1 = 0.2532, wR_2 = 0.1605$
Goodness-of-fit	1.056
Largest difference peak and	0.588 and -0.406
hole (e $Å^{-3}$)	

cyanotriphenylborate compound, but slightly shorter than those in the isocyanide cationic ones as well as in the cyanamide and phosphaalkyne complexes *trans*-[FeH(NCNH₂)(dppe)₂][BF₄] and *trans*-[FeH(η^1 -P= CBu^t)(dppe)₂][BPh₄] (2.244(4) Å [44a] and 2.276(2) Å [44b], respectively). These differences conceivably result from a stronger π -electron releasing ability of the metal in the neutral centres in comparison with that in the cationic ones.

The Fe–H1 distance, 1.65(9) Å, is higher than those reported in the aforementioned cases and than the expected value, 1.53 Å, based on the sum of the iron and hydrogen covalent radii, suggesting a significant *trans* influence of the cyanide ligand.

Preliminary electrochemical studies corroborate the di and tri-nuclear characters of complexes 4 and 5 (6 and 7 could not be studied due to their instability in the electrolytic medium, even at low temperatures), respectively.

In fact, those complexes exhibit, by cyclic voltammetry, in 0.2 M [NBu₄][BF₄]/CH₂Cl₂, not only the expected reversible single-electron oxidation waves due to the Fe^{II} \rightarrow Fe^{III} oxidations, at $E_{1/2}^{\text{ox}}$ in the 0.43–0.70 V (vs. SCE) range, i.e. higher than that observed for the related complex *trans*-[FeH(CN)(dppe)₂] (0.33 V [17]) and lower than that for *trans*-[FeH(CNR)(dppe)₂]⁺ (0.87 V (R = Me) or 0.90 V (R = Et) [45,46]), but also irreversible reduction waves at E_p^{red} in the range from -1.0 to -1.5 V assigned to reductions centred at the other metal centres. This is in accord with the detection of irreversible cathodic waves (in the -0.5 to -1.5 V range) for the corresponding transition metal Lewis acid sources [PdCl₂(PPh₃)₂] and [ReOCl₃(PPh₃)₂].

Interestingly, the observation of two distinct iron(II) centred oxidation waves for the trinuclear complex 5 is indicative [47–50] of an iron–iron interaction between the two iron centres through the {CN-Re-CN} bridging moiety. The details of the electrochemical behaviours of such complexes will be reported separately.

3. Final comments

This work shows that *trans*-[FeH(CN)(dppe)₂] constitutes a convenient source of a cyano-iron centre with both Brönsted and Lewis basic properties, providing a promising and easily accessible building block for the synthesis of cyano-bridged complexes, including mixed valent compounds, and for the generation in situ of isocyanide ligands which are not easily accessible by pure organic methods. The study also indicates that the cyano-binding metal site *trans*-{ $FeH(dppe)_2$]⁺, which is a sufficient π -electron-donor to ligate N₂, can readily activate cyanide towards a variety of electrophiles such as those shown above. Preliminary electrochemical (cyclic voltammetric) results also indicate that the cyano-bridge can allow the electronic communication between the metal atoms, a possibility that deserves further exploration namely towards the generation of mixed valence Fe^{II}/Fe^{III} complexes.

4. Experimental

4.1. General

All the reactions were carried out under argon and using standard inert gas flow and vacuum techniques. Solvents were purified by standard procedures. *trans*-[FeH(CN)(dppe)₂] [51], [PtCl(Ph)(PPh₃)₂] [52] and [WCl₄(PPh₃)₂] [53] were prepared according to published procedures. [PdCl₂(PPh₃)₂], [ReOCl₃(PPh₃)₂], Me₃SiI, MeI, [Et₃O]BF₄ and PhCOCl were commercially available.

Infrared (IR) measurements were carried out in KBr pellets (values in cm⁻¹; intensity of bands is referred as m = medium, s = strong) on a Perkin–Elmer 683 and a Bio-Rad FTS 3000 spectrophotometers and ¹H, ³¹P{¹H} and ¹³C NMR spectra on a Varian Unity 300 spectrometer. Chemical shifts are in ppm relative to SiMe₄ (¹H and ¹³C) or P(OMe)₃ (³¹P) (s = singlet, d = doublet, t = triplet, q = quartet, qt = quintet, m = multiplet, br = broad). Positive-ion FAB mass spectra were obtained on a Trio 2000 instrument by bombarding 3-nitrobenzyl alcohol (NBA) matrixes of the samples with 8 keV (ca. 1.28×10^5 J) Xe atoms. Mass calibration for data system acquisition was achieved using CsI. Elemental analyses were carried out at the Laboratório de Análises of the Instituto Superior Técnico.

The electrochemical experiments were performed on an EG&G PAR 173 potentiostat and an EG&G PARC 175 universal programmer, or on a EG&G PARC 273 potentiostat/galvanostat connected to a PC computer through a GPIB interface (National Instruments PC-2A). A two-compartment three-electrode cell, with a platinum-wire working electrode, probed by a Luggin capillary connected to a silver wire pseudo-reference electrode and a platinum auxiliary electrode, was employed. The electrochemical experiments were performed in a N_2 atmosphere at room temperature (r.t.). The potentials were measured by CV in 0.2 mol dm^{-3} [NBu₄][BF₄]/CH₂Cl₂ and the values are quoted relative to the saturated calomel electrode (SCE) by using the *trans*-[FeHCl(dppe)₂]^{0/+} or the [Fe(η^5 -C₅H₅)₂]^{0/+} redox couples ($E_{1/2}^{\text{ox}} = -0.143$ or 0.525 V vs. SCE, in CH₂Cl₂, respectively) as the internal standards.

4.2. Syntheses

4.2.1. trans-[$HFe(CNCOC_6H_5)(dppe)_2$]Cl (1)

To a CH_2Cl_2 solution (10 cm³) of *trans*-[FeH(CN)(dppe)₂] (0.030 g, 0.034 mmol), C₆H₅COCl (0.11 mmol in a 1:10 CH₂Cl₂ dilution of the pure compound) was added and the mixture was left stirring overnight. The solution was then concentrated under vacuum and upon addition of Et₂O complex **1** precipitated as an orange solid which was separated by filtration, washed with Et_2O and dried in vacuum (ca. 0.015 g, 45% yield).

IR: $v_{\rm CN}/v_{\rm CO}$ 1881s and 1838s cm⁻¹. NMR: ¹H (CD₂Cl₂): δ 7.67–6.93 (m, 45H, $H_{\rm arom}$), 2.72 (s,br, 4H, CH₂), 2.23 (s,br, 4H, CH₂), -7.45 (qt, ²J_{HP} = 47.0 Hz, 1H, Fe–H). ³¹P{¹H} (CD₂Cl₂): δ – 59.31. FAB⁺ -MS: m/z 985 [M]⁺. Anal. Calc. for C₆₀H₅₄NOClP₄Fe·4CH₂Cl₂: C, 56.49; H, 4.60; N, 1.03. Found: C, 56.69; H, 4.70; N, 1.00%.

4.2.2. $trans-[FeH(CNMe)(dppe)_2]I(2)$ and $trans-[FeH(CNEt)(dppe)_2][BF_4](3)$

These complexes were prepared by treatment of a CH_2Cl_2 or THF solution of *trans*-[FeH(CN)(dppe)₂] with MeI or [Et₃O][BF₄], respectively (in a 1:1.1 molar ratio). The reaction solution was left stirring at r.t. for 48 (2) or 12 h (3) and then was concentrated under vacuum followed by addition of a precipitating solvent (n-pentane or Et₂O). The final solid thus obtained was separated by filtration, washed with n-pentane or Et₂O and dried under vacuum (typically, 30–60% yields). The characterisation data for these complexes are identical to those previously described [41,42] and will not be repeated.

4.2.3. $[HFe(dppe)_2(\mu-CN)PdCl_2(PPh_3)]$ (4)

To a THF solution (15 cm^3) of trans- $[FeH(CN)(dppe)_2]$ (0.030 g, 0.034 mmol), $[PdCl_2(PPh_3)_2]$ (0.026 g, 0.037 mmol) was added and the mixture was left stirring overnight whereafter it was concentrated in vacuum. Dropwise addition of Et₂O led to the formation of an oil. Isolation of this oily residue by decantation of the supernatant solution, addition of Et₂O followed by the application of the freeze-thaw technique and vigorous stirring resulted in the formation of an orange powder of 4 which was separated by filtration, washed with Et_2O and dried in vacuum (ca. 0.020 g, 45%) yield). In several attempts to perform this reaction in CH₂Cl₂ the same compound could be obtained, although in much lower yields.

IR: $v_{C\equiv N}$ 2074 cm⁻¹. NMR: ¹H (CD₂Cl₂): δ 7.93– 7.01 (m, 55H, H_{arom}); 2.53 (s,br, 4H, C H_2), 1.90 (s,br, 4H, C H_2), -13.79 (qt, ² J_{HP} = 46.1 Hz, 1H, Fe–H). ³¹P{¹H} (CD₂Cl₂): δ – 50.05 (dppe); -112.84 and – 117.02 (PPh₃) (see text). FAB⁺ -MS: m/z 1020 [M – PPh₃ – Cl]⁺, 630 [Fe(dppe)PdCl₂]⁺, 596 [Fe(dppe)PdCl]⁺. Anal. Calc. for C₇₁H₆₄Cl₂NP₅PdFe· 2CH₂Cl₂: C, 58.86; H, 0.94; N, 4.34. Found: C, 58.57; H, 5.10; N, 1.11%.

4.2.4. $[{HFe(dppe)_2(\mu-CN)}_2(ReOCl_3)]$ (5)

To a CH_2Cl_2 solution (13 cm³) of *trans*-[FeH(CN)(dppe)₂] (0.031 g, 0.035 mmol), [Re-OCl₃(PPh₃)] (0.021 g, 0.025 mmol) was added and the mixture was left stirring overnight. It was then concentrated in vacuum and n-pentane was added, whereupon a purple solid of complex **6** precipitated which was separated by filtration, washed with n-pentane and dried in vacuum (ca. 0.026 g, 36% yield).

IR: $v_{C=N}$ 2010s cm⁻¹, $v_{ReO} = 900$ w cm⁻¹ NMR: ¹H (CD₂Cl₂): δ 7.56–6.97 (m, 80H, H_{arom}); 2.84 (s,br, 8H, CH₂), 2.32 (s,br, 8H, CH₂); -13.08 (qt, ²J_{HP} = 46.94 Hz, 2H, Fe–H). ³¹P{¹H} (CD₂Cl₂): δ -51.20. ¹³C{¹H} (CD₂Cl₂): δ 148.65 (CN). FAB⁺ -MS: m/z 1015 [{ReOCl₃}₂(dppe)]⁺, 640 [Fe(dppe)Re]⁺, 617 [{ReOCl₃}₂]⁺, 308 [ReOCl₃]⁺. Anal. Calc. for C₁₀₆H₉₈Cl₃N₂OP₈ReFe₂: C, 61.54; H, 4.76; N, 1.35. Found: C, 62.00; H, 4.65; N, 1.32%.

4.2.5. $[{HFe(dppe)_2(\mu-CN)}_2PtCl(Ph)]$ (6)

To a CH_2Cl_2 solution (15 cm³) of trans- $[FeH(CN)(dppe)_2]$ (0.030 0.034 mmol), g, [Pt(Ph)Cl(PPh₃)₂] (0.013 g, 0.015 mmol) was added. The mixture was left stirring overnight whereafter it was concentrated under vacuum, Et₂O was added and the mixture was cooled to -18 °C for approximately 8 h. The white solid of PPh₃ thus formed was filtered off and discarded. Further addition of Et₂O led to the precipitation of complex 6 as a greenish yellow solid which was separated by filtration, washed with Et₂O and dried in vacuum (ca. 0.025 g, 35% yield).

IR: $v_{C=N}$ 2044 cm⁻¹. NMR: ¹H (CD₂Cl₂): δ 7.39– 6.99 (m, 85 H, H_{arom}), 2.48 (s,br, 8H, CH_2), 2.01 (s,br, 8H, CH_2), -14.55 (m,br 2H, Fe-H). ³¹P{¹H} (CD₂Cl₂): δ -52.58. FAB⁺ -MS: m/z 1757 [{Fe(CN)(dppe)₂}₂]⁺, 880 [FeH(CN)(dppe)₂]⁺, 471 [Fe(CN)Pt(Ph)Cl(CN) Fe]⁺, 360 [Pt(Ph)Cl(CN)₂]⁺, 307 [Pt(Ph)Cl)]⁺. *Anal*. Calc. for C₁₁₂H₁₀₃ClN₂P₈PtFe₂·3CH₂Cl₂: C, 59.47; H, 4.48; N, 1.21. Found: C, 59.02; H, 4.91; N, 0.83%.

4.2.6. $[{XFe(dppe)_2(\mu-CN)}_2WCl_3(OH)]$ (7)

To a THF solution (10 cm³) of *trans*-[FeH(CN)(dppe)₂] (0.030 g, 0.034 mmol), [WCl₄(PPh₃)₂] (0.030 g, 0.037 mmol) was added. The mixture was left stirring overnight whereafter it was taken to dryness leading to the formation of an oily residue. Addition of Et₂O followed by the application of the freeze–thaw technique and vigorous stirring resulted in the formation of a violet powder of 7 that was separated by filtration, washed with Et₂O and dried under vacuum. Purple crystals used for X-ray analysis were grown on recrystallisation from CH₂Cl₂/Et₂O (ca. 0.031 g, 40% yield).

IR: $v_{C=N}$ 1988 cm⁻¹. Paramagnetic. *Anal*. Calc. for $C_{106}H_{97}Cl_3N_2P_8WFe_2X_2$ (X = Cl): C, 59.5; H, 4.58; N, 1.31. Found: C, 58.7; H, 4.99; N, 1.19%.

4.3. X-ray measurements and structure determination

Crystal data and refinement details are given in Table 2. The crystal was mounted on glass fibre and then flash-frozen to 100 K (Oxford Cryosystem-Cryostream

Cooler). Preliminary examination and intensities data collections were carried out on a Kuma KM4CCD ĸaxis diffractometer with graphite-monochromated Mo K α radiation. Crystal was positioned at 65 mm from the KM4CCD camera. 612 frames were measured at 0.75° intervals with a counting time of 35 s. The data were corrected for Lp. Data reduction and analysis were carried out with the Kuma Diffraction (Wroclaw) programs [54]. The structures were solved by direct methods (program SHELXS-97 [55]) and refined by the full-matrix least-squares method on all F^2 data using the SHELXL-97 programs [56]. The hydride H atom was located in a difference electron density map and its position and isotropic displacement parameter were refined. All other H atoms were positioned with ideal geometry and refined with fixed individual isotropic displacement parameters.

5. Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no CCDC 207288. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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