Synthesis, Reactivity, and Molecular Structures of Bis(diphenylphosphanyl)amine- and Bis(diphenylphosphanyl)amide-Bridged Heterobimetallic μ-Isonitrile- and μ-Aminocarbyne Complexes (*Fe*−*Pt*)

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Addition of isonitriles to $[(OC)_3Fe(\mu\text{-}CO)(\mu\text{-}Ph_2PNHPPh_2)Pt(PPh_3)]$ **1** produces the μ-isonitrile complexes $[(OC)_3Fe(\mu\text{-}C{=}NR)(\mu\text{-}Ph_2PNHPPh_2)Pt(PPh_3)]$ **2**, which are transformed to the μ-aminocarbyne complexes $[(OC)_3Fe\{\mu\text{-}CN(El)R\}(\mu\text{-}Ph_2PNHPPh_2)Pt(PPh_3)]^+$ **3** and **4** by electrophilic addition of $[El][BF_4]$ or $[El][OSO_2CF_3]$ (El = H, Me). The dppa backbone of **4** is readily deprotonated by $KOSiMe_3$ to yield the very stable zwitterionic aminocarbyne complex $[(OC)_3Fe\{\mu\text{-}CN(Me)2,6\text{-}xylyl\}(\mu\text{-}Ph_2PNPPh_2)Pt(PPh_3)]$ **5**.

Isonitriles (RNC) are often employed as ligands in coordination chemistry, since steric and electronic variation of the group R permits a fine tuning of the properties of a metal complex.[1][2] In addition to the innumerable examples of mononuclear isonitrile complexes, many heterobimetallic complexes and higher-nuclearity clusters bearing *terminal* isonitrile ligands have now been documented. However, polymetallic systems containing an isonitrile bridge between *two different* metal centers are still extremely scarce.[3a][3b][3c] We recently obtained the bis(diphenylphosphanyl)methane-bridged μ-isonitrile complex $[(OC)_3Fe(\mu\text{-}C{=}N\text{-}xylyl)(\mu\text{-}dppm)Pt(PPh_3)]$ by treatment of $[(OC)_3Fe\{Si(OMe)_3\}(\mu\text{-}dppm)Pt(H)(PPh_3)]$ with 2,6-dimethylphenylisonitrile under formal loss of $HSi(OMe)_3$.[3c] We report here on a different route for the synthesis of the bis(diphenylphosphanyl)amine-bridged μ-isonitrile complexes $[(OC)_3Fe(\mu\text{-}C{=}NR)(\mu\text{-}dppa)Pt(PPh_3)]$ and on their transformation to μ-aminocarbyne complexes, which have been characterized by multinuclear NMR techniques and single-crystal X-ray diffraction studies.

Results

In a manner similar as described by Shaw. et al. for the synthesis of the dppm-bridged complex $[(OC)_3Fe(\mu\text{-}CO)(\mu\text{-}dppm)Pt(PPh_3)]$[4], we obtained the dppa-bridged analogue $[(OC)_3Fe(\mu\text{-}CO)(\mu\text{-}dppa)Pt(PPh_3)]$ **1** containing a μ-carbonyl ligand by reaction of $[(OC)_4Fe(dppa\text{-}P)]$[5] with $[Pt(H_2C{=}CH_2)(PPh_3)_2]$ in 79% yield, as shown in Scheme 1. Addition of *o*-anisylisonitrile or 2,6-xylylisonitrile in a 1:1 ratio to the latter complex yields *selectively* within 10 min. at ambient temperature the heterobimetallic species $[(OC)_3Fe(\mu\text{-}C{=}NR)(\mu\text{-}dppa)Pt(PPh_3)]$ (**2a**: R = 2,6-xylyl; **2b**: R = *o*-anisyl) by substitution of the bridging carbonyl in **1**. There was no indication for a competing formation of an isomer bearing a terminal isonitrile ligand.

The most significant change in the IR spectra that accompanies the conversion of **1** to **2** is the replacement of the ν(CO) stretch of the bridging carbonyl of **1** (1761 cm^{-1}) by a broadened ν(C=N) stretch of medium intensity (**2a**: 1674; **2b**: 1670 cm^{-1}). The latter bands fall in the typical range for bridging isonitrile ligands with a strongly *bent* C=N−R group. The $^{31}P\{^1H\}$-NMR spectra of all the compounds reported herein characteristically show three mutually coupled resonances, as exemplified by that of **2a**. The spectrum of this μ-isonitrile complex features a doublet of doublets at $\delta = 114.3$, attributable to the iron-bound dppa-phosphorus atom, which shows a strong coupling $[^{2+3}J(P{-}P) = 174\ Hz]$ to the platinum-bound dppa phosphorus at $\delta = 90.3$. These signals are split further due to the presence of the PPh_3 ligand. The latter gives rise to a doublet of doublets at $\delta = 40.4$, with couplings of 44 and 6 Hz. All signals are flanked by ^{195}Pt satellites, the Pt−P couplings of which are also evident in the ^{195}Pt-NMR spectrum (see Experimental Section).

Addition of excess of $HBF_4\cdot Et_2O$ or $HOSO_2CF_3$ to a solution of **2** in dichloromethane led instantaneously to formation of the stable *N*-protonated cationic μ-aminocarbyne complexes $[(OC)_3Fe\{\mu\text{-}CN(H)R\}(\mu\text{-}dppa)Pt(PPh_3)][X]$ (**3a**: R = 2,6-xylyl, X = BF_4^-; **3b**: R = *o*-anisyl, X = $OSO_2CF_3^-$) in almost quantitative yields. It seems that in

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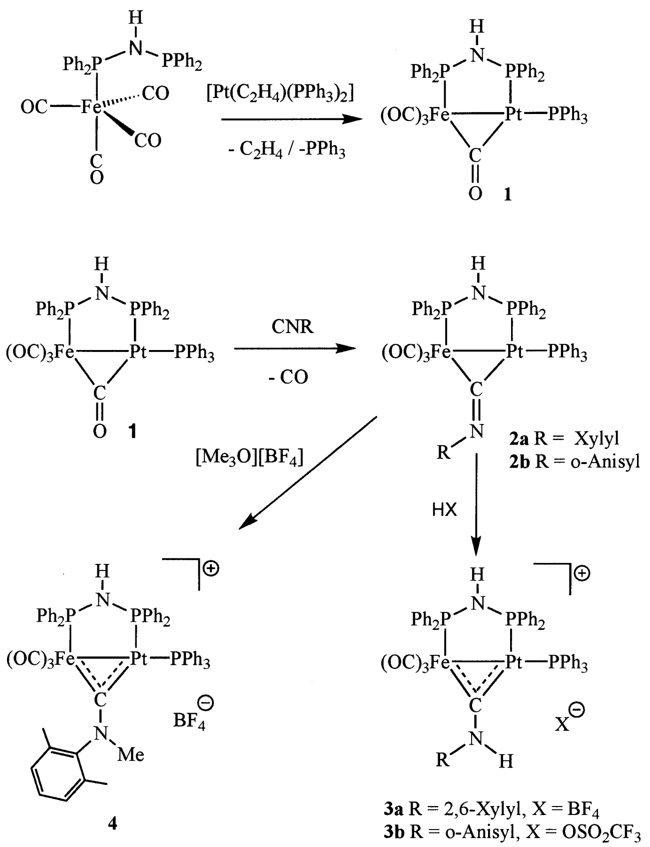
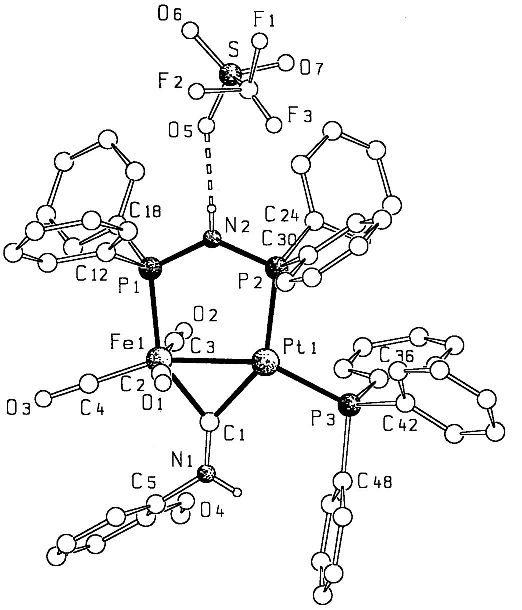
Scheme 1



this case protonation of the nitrogen atom of the μ-CNR ligand is preferred to protonation of the metal-metal bond or a metal center yielding a heterometallic hydride complex, a reaction which would be a priori also conceivable. For example, protonation of [(OC)$_3$Fe(μ-CO)(μ-dppm)Pt(PPh$_3$)] with HBF$_4$ is reported to give the cationic hydride-complex [(OC)$_4$Fe(μ-dppm)Pt(H)(PPh$_3$)][BF$_4$].[4]

The spectroscopic data obtained in solution were in agreement with the results of a single-crystal X-ray diffraction study performed on **3b**. The latter shows that the μ-aminocarbyne ligand symmetrically bridges [Fe−C(1) 1.975(6), Pt−C(1) 1.923(5) Å] the two metal centers, the separation of which, 2.5282(10) Å, is indicative of the presence of a metal-metal bond. Due to steric factors, only the isomer with the anisyl group oriented towards the iron center is formed. The short bond length between C(1) and N(1) of 1.263(7) Å reflects the partial C=N double-bond character of the μ-aminocarbyne unit, which, therefore, may alternatively be considered as a dimetallated iminium salt ligand. To date, to the best of our knowledge, only one other example of a *heterobimetallic* μ-aminocarbyne complex has been structurally described. A C−N distance of 1.29(2) Å was observed for this tungsten-gold complex bridged by a CN(Et)Me ligand.[6] The triflate counterion of **3b** is hydrogen-bonded to the N−H group {*d*[N(2)−H(2)...O(5)] 2.867 Å; H(2)···O(5) 2.10(7) Å} of the dppa ligand. The position of H(2) could be located and was isotropically refined. A comparable distance of 2.91 Å has been reported by Ellermann et al. for the hydrogen-bridged complex [Cu(CN)(dppa)PPh$_3$]·MeOH.[7] Overall, the structure of **3b** shows strong similarities to that of the recently published μ-vinylidene complex [(OC)$_3$Fe{μ-C=C(H)Ph}(μ-dppm)Pt(PPh$_3$)].[8]

Figure 1. View of the crystal structure of **3b** showing the atom-numbering scheme[a]



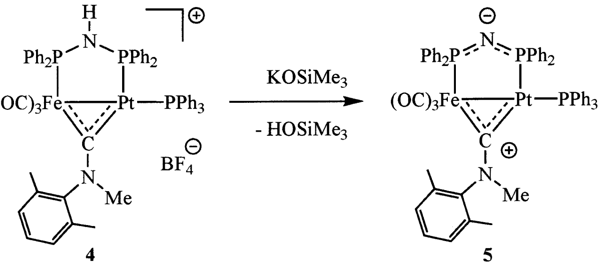
[a] Selected bond lengths [Å] and angles [°]: Fe−Pt 2.528(1), Fe−P(1) 2.226(3), Pt−P(2) 2.327(2), Pt−P(3) 2.291(1), Fe−C(1) 1.975(6), Pt−C(1) 1.923(5), C(1)−N(1) 1.263(7), P(1)−N(2) 1.668(9), P(2)−N(2) 1.697(9); C(1)−N(1)−C(5) 126.1(5), Pt−C(1)−Fe 80.9(2), Fe−Pt−C(1) 48.7(2), Pt−Fe−C(1) 50.5(2), C(1)−Fe−P(1) 146.9(2), C(1)−Pt−P(2) 144.2(2), C(1)−Pt−P(3) 103.5(2), P(1)−Fe−Pt 96.45(5), P(2)−Pt−P(3) 112.18(5), Fe−Pt−P(3) 151.32(4), P(1)−N(2)−P(2) 126.9(3).

In a similar manner, upon treatment of **2a** with a slight excess of [Me$_3$O][BF$_4$], electrophilic addition affords the stable *N*-alkylated product [(OC)$_3$Fe{μ-CN(Me)xylyl}(μ-dppa)Pt(PPh$_3$)][BF$_4$] **4**, which has been fully characterized by multinuclear NMR techniques and elemental analysis. Characteristic for this type of aminocarbyne complex is the ^{13}C resonance of the μ-C atom, which is observed in the lowfield region at $\delta = 311.7$ as a doublet of doublets of doublets with ^2J(P−C) coupling constants of 3, 11, and 82 Hz. Upon treatment of **3** with weak bases such as NEt$_3$ or KOSiMe$_3$, deprotonation of the μ-aminocarbyne ligand yields the precursor compounds **2**.

However, addition of KOSiMe$_3$ to a solution of **4** did not yield the anticipated μ-siloxycarbene complex.[9] Instead, deprotonation of the dppa backbone occurred, with formation of the stable zwitterionic μ-aminocarbyne complex [(OC)$_3$Fe{μ-CN(Me)xylyl}(μ-Ph$_2$PNPPh$_2$)Pt(PPh$_3$)] **5**.

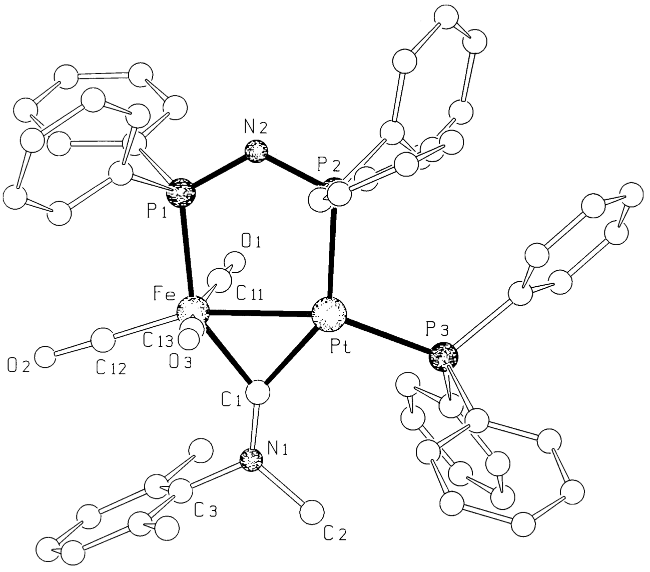
In addition to a detailed spectroscopic investigation in solution (see Experimental Section), the solid-state structure of **5** has been determined by a single-crystal X-ray diffraction study. Comparison with the structure of **3b** reveals that deprotonation of the dppa backbone has no significant influence on the metal-metal [Fe−Pt 2.517(1) Å] and metal-

Scheme 2



phosphorus distances. Only the shortened P(1)−N(2) and P(2)−N(2) distances of 1.608(4) and 1.633(4) Å may reflect a charge delocalization in the bis(diphenylphosphanyl)amide bridge. These values are comparable to the P−N distances [1.626(7) and 1.598(7) Å] found in the bis(diphenylphosphanyl)amide-bridged dinuclear complex [Co_2(μ-CO)$(CO)_4$(μ-Ph_2PNPPh_2)(μ-PPh_2)] and the mononuclear chelate [Pd(Cl)(Ph_2PNPPh_2)(PEt_3)], as reported recently by Ellermann[10] and Muller.[11] Compared to the P−N−P angle of **3b** [126.9(3)°], that of **5** is somewhat more acute and amounts to 123.4(2)°.

Figure 2. View of the crystal structure of **5** showing the atom-numbering scheme[a]



[a] Selected bond lengths [Å] and angles [°]: Fe−Pt 2.517(1), Fe−P(1) 2.276(2), Pt−P(2) 2.349(2), Pt−P(3) 2.277(1), Fe−C(1) 1.918(4), Pt−C(1) 1.996(5), C(1)−N(1) 1.296(6), P(1)−N(2) 1.608(4), P(2)−N(2) 1.633(4); C(1)−N(1)−C(2) 124.6(4), Pt−C(1)−Fe 80.0(2), Fe−Pt−C(1) 48.6(1), C(1)−Fe−Pt 51.3(2), C(1)−Fe−P(1) 146.9(2), C(1)−Pt−P(2) 141.40(13), C(1)−Pt−P(3) 109.5(1), P(1)−Fe−Pt 95.60(5), P(2)−Pt−P(3) 108.97(5), Fe−Pt−P(3) 157.14(4), P(1)−N(2)−P(2) 123.4(5).

To the best of our knowledge, the solid-state structures of **3b** and **5** represent the first examples of X-ray crystal-structure determinations performed on heterometallic bis(diphenylphosphanyl)amine- and bis(diphenylphosphanyl)amide-bridged systems. We are currently investigating the steric and electronic factors that govern the bonding mode of the coordinated isonitrile ligand (bridging vs. terminal)[12] and the reactivity of the amide bridge of [$(OC)_3$Fe{μ-CN(R)(R′)}(μ-Ph_2PNPPh_2)Pt(PPh_3)] towards electrophiles. Preliminary results using an $[AuPPh_3]^+$ fragment indicate that this route permits the synthesis of heterotrimetallic μ-aminocarbyne complexes of the type [$(OC)_3$(L)Fe{μ-CN(R)(R′)}{μ-Ph_2PN($AuPPh_3$)PPh_2}Pt(PPh_3)$]^+$ (L = CO, CNR).

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Experimental Section

All reactions were performed in Schlenk-tube flasks under purified nitrogen. Solvents were dried and distilled under nitrogen before use, toluene and hexane over sodium, dichloromethane from P_4O_{10}. Nitrogen was passed through BASF R3-11 catalyst and molecular-sieve columns to remove residual oxygen and water. Elemental C, H and N analyses were performed on a Leco Elemental Analyser CHN 900. − The ^{1}H-, $^{31}P\{^{1}H\}$-, and $^{13}C\{^{1}H\}$-NMR spectra were recorded at 200.13, 81.01 and 50.32 MHz, respectively, on a Bruker ACP 200 instrument. Phosphorus-chemical shifts were referenced to 85% H_3PO_4 in H_2O with downfield shifts reported as positive. ^{195}Pt-chemical shifts were measured on a Bruker ACP 200 instrument (42.95 MHz) and externally referenced to K_2PtCl_4 in water with downfield chemical shifts reported as positive. NMR spectra were recorded in pure $CDCl_3$, unless otherwise stated. The presence and amount of CH_2Cl_2 retained in **3a** and **4** was determined from the ^{1}H-NMR spectra. − The reactions were generally monitored by IR spectroscopy in the ν(CO) region. − [Me_3O][BF_4] and 2,6-xylylisonitrile were obtained from Aldrich and Fluka and were used as received; dppa was prepared as described by Meinel and Nöth.[13]

Preparation of [(CO)₃Fe(μ-CO)(μ-dppa)Pt(PPh₃)] (**1**): To a solution of [Pt($H_2C{=}CH_2$)$(PPh_3)_2$] (751 mg, 1.0 mmol) in toluene (10 ml) one equivalent of [$(OC)_4$Fe(dppa-*P*)] (553 mg, 1.0 mmol) was added. After stirring for 20 min. at ambient temperature, the orange-red solution was concentrated and **1** was precipitated by slow addition of hexane. The resulting crude yellow-orange product, which was sufficiently pure for further reactions, was then dried in vacuo. Yield: 798 mg (79%). Analytically pure **1** was obtained in form of red-orange crystals by recrystallization from toluene/Et_2O. − IR (KBr): $\tilde{\nu}$ = 2006 cm^{-1} (s), 1939 (vs), 1925 (sh), 1761 (m, br.) ν(CO). − ^{1}H NMR: δ = 4.97 [m, br., NH, ^{3}J(Pt−H) = 95.0 Hz], 7.00−7.69 (m, 35 H, phenyl). − $^{31}P\{^{1}H\}$ NMR: δ = 118.1 [dd, P^1(Fe), $^{2+3}J(P^1{-}P^2)$ = 213, $^{3+4}J(P^1{-}P^3)$ = 4, ^{2+3}J(Pt−P) = 30 Hz], 93.4 [dd, P^2(Pt), ^{1}J(Pt−P) = 2877 Hz], 42.0 [dd, P^3(Pt), $^{2}J(P^2{-}P^3)$ = 63, ^{1}J(Pt−P) = 4628 Hz]. − $^{195}Pt\{^{1}H\}$NMR: δ = −2543 [ddd, $^{2+3}J(Pt{-}P^1)$ = 30, $^{1}J(Pt{-}P^2)$ = 2877, $^{1}J(Pt{-}P^3)$ = 4628 Hz]. − $C_{46}H_{36}FeNO_4P_3Pt \cdot Et_2O$ (1010.65 + 74.12): calcd. C 55.36, H 4.27, N 1.29; found C 55.48, H 4.04, N 1.08.

Preparation of [(CO)₃Fe(μ-CN-xylyl)(μ-dppa)Pt(PPh₃)] (**2a**): To a solution of **1** (202 mg, 0.2 mmol) in CH_2Cl_2 (5 ml), one equivalent of 2,6-xylylisonitrile, dissolved in CH_2Cl_2 (5 ml), was added dropwise. After stirring for 15 min. at ambient temperature (evolution of CO), the orange-red solution was concentrated and **2a** was precipitated by the slow addition of hexane. The resulting microcrystalline yellow-orange product was dried in vacuo. Yield: 194

mg (87%). – IR (CH_2Cl_2): $\tilde{\nu}$ = 2004 cm^{-1} (s), 1934 (vs) ν(CO); 1671 (m, br.) ν(CN). – IR (KBr): $\tilde{\nu}$ = 3270 cm^{-1} (w) ν(NH); 2000 (m), 1934 (s), 1922 (s) ν(CO); 1674 (m, br.) ν(C=N). – ^{1}H NMR: δ = 2.07 (s, 3 H, xylyl-CH_3), 4.96 [m, br., NH, ^{3}J(Pt–H) = 89.0 Hz], 6.84–7.88 (m, 38 H, phenyl). – ^{31}P{^{1}H} NMR: δ = 114.3 [dd, P^{1}(Fe), ^{2+3}J(P^{1}–P^{2}) = 174, ^{3+4}J(P^{1}–P^{3}) = 6, ^{2+3}J(Pt–P) = 50 Hz], 90.3 [dd, P^{2}(Pt), ^{1}J(Pt–P) = 2866 Hz], 40.4 [dd, P^{3}(Pt), ^{2}J(P^{2}–P^{3}) = 44, ^{1}J(Pt–P) = 4326 Hz]. – ^{195}Pt{^{1}H}NMR: δ = −2678 [ddd, ^{2+3}J(Pt–P^{1}) = 50, ^{1}J(Pt–P^{2}) = 2856, ^{1}J(Pt–P^{3}) = 4328 Hz]. – $C_{54}H_{45}FeN_2O_3P_3Pt$ (1113.82): calcd. C 58.23, H 4.07, N 2.51; found C 58.26, H 3.86, N 2.70.

Preparation of [(CO)$_3$Fe(μ-CN-o-anisyl)(μ-dppa)Pt(PPh$_3$)] (**2b**): This yellow derivative was prepared and isolated as described for **2a**. – IR (CH_2Cl_2): $\tilde{\nu}$ = 2008 cm^{-1} (m), 1940 (s) ν(CO); 1670 (m, br.) ν(C=N). – IR (KBr): $\tilde{\nu}$ = 3224 cm^{-1} (w) ν(NH); 2003 (m), 1933 (s) ν(CO); 1669 (m, br.) ν(C=N). – ^{1}H NMR: δ = 3.71 (s, 3 H, OCH_3), 5.04 [m, br., NH, ^{3}J(Pt–H) = 89.8 Hz], 6.75–7.75 (m, 39 H, phenyl). – ^{31}P{^{1}H} NMR: δ = 113.4 [dd, P^{1}(Fe), ^{2+3}J(P^{1}–P^{2}) = 173, ^{3+4}J(P^{1}–P^{3}) = 9, ^{2+3}J(Pt–P) = 40 Hz], 89.3 [dd, P^{2}(Pt), ^{1}J(Pt–P) = 2884 Hz], 40.0 [dd, P^{3}(Pt), ^{2}J(P^{2}–P^{3}) = 45, ^{1}J(Pt–P) = 4262 Hz]. – ^{195}Pt{^{1}H} NMR: δ = −2688 [ddd, ^{2+3}J(Pt–P^{1}) = 40, ^{1}J(Pt–P^{2}) = 2886, ^{1}J(Pt–P^{3}) = 4264 Hz]. – $C_{53}H_{43}FeN_2O_4P_3Pt$ (1115.79): calcd. C 57.05, H 3.88, N 2.51; found C 56.69, H 4.16, N 2.29.

Preparation of [(CO)$_3$Fe{μ-CN(H)xylyl}(μ-dppa)Pt(PPh$_3$)]-[BF$_4$] (**3a**): This complex was prepared by adding excess HBF_4ÆEt$_2$O to a solution of **2a** (0.111 g, 0.1 mmol) in CH_2Cl_2 (10 ml) at 253 K. After warming to ambient temperature, all volatiles were removed under reduced pressure. The orange-red residue was rinsed with Et_2O (3 ml) and dried in vacuo. – IR (CH_2Cl_2): $\tilde{\nu}$ = 2041 cm^{-1} (m), 1981 (vs) ν(CO); 1527 (w) ν(CN). – ^{1}H NMR: δ = 2.10 (s, 6 H, xylyl-CH_3), 6.53 [m, br., NH, ^{3}J(Pt–H) = 85 Hz], 6.85–7.85 (m, 38 H, phenyl), 9.08 (m, br., NH). – ^{31}P{^{1}H} NMR: δ = 103.6 [dd, P^{1}(Fe), ^{2+3}J(P^{1}–P^{2}) = 99, ^{3+4}J(P^{1}–P^{3}) = 13, ^{2+3}J(P^{1}–Pt) = 71 Hz], 80.5 [dd, P^{2}(Pt), ^{2}J(P^{2}–P^{3}) = 13, ^{1}J(P^{2}–Pt) = 2889 Hz], 37.2 [t, P^{3}(Pt), ^{1}J(P^{3}–Pt) = 3810 Hz]. – $C_{54}H_{46}BF_4FeN_2O_3P_3Pt \cdot 1.5\ CH_2Cl_2$ (1201.63 + 127.40): calcd. C 49.93, H 3.73, N 2.12; found C 49.99, H 3.88, N 2.20.

Preparation of [(CO)$_3$Fe{μ-CN(H)-o-anisyl}(μ-dppa)Pt-(PPh$_3$)][BF$_4$] (**3b**): This complex was prepared by adding excess $HOSO_2CF_3$ to a solution of **2b** (0.112 g, 0.1 mmol) in CH_2Cl_2 (10 ml) at 253 K. After warming to ambient temperature, all volatiles were removed under reduced pressure. The orange-red residue was rinsed with Et_2O (3 ml) and dried in vacuo. – IR (CH_2Cl_2): $\tilde{\nu}$ = 2042 cm^{-1} (m), 1979 (vs) ν(CO); 1532 (w) ν(CN). – ^{1}H NMR: δ = 3.67 (s, 3 H, OCH_3), 6.94 [m, br., NH, ^{3}J(Pt–H) = 84 Hz], 6.87–7.42 (m, 39 H, phenyl), 7.91 (m, br., NH). – ^{31}P{^{1}H} NMR: δ = 102.2 [dd, P^{1}(Fe), ^{2+3}J(P^{1}–P^{2}) = 99, ^{3+4}J(P^{1}–P^{3}) = 14, ^{2+3}J(P^{1}–Pt) = 73 Hz], 79.0 [dd, P^{2}(Pt), ^{2}J(P^{2}–P^{3}) = 12, ^{1}J(P^{2}–Pt) = 2868 Hz], 37.3 [dd, P^{3}(Pt), ^{1}J(P^{3}–Pt) = 3791 Hz]. – ^{195}Pt{^{1}H} NMR: δ = −2510 [ddd, ^{2+3}J(P^{1}–Pt) = 73, ^{1}J(P^{2}–Pt) = 2868, ^{1}J(P^{3}–Pt) = 3791 Hz]. – $C_{54}H_{44}F_3FeN_2O_7P_3PtS$ (1265.83): calcd. C 50.18, H 3.70, N 2.17; found C 51.23, H 3.51, N 2.21.

Preparation of [(CO)$_3$Fe{μ-CN(Me)xylyl}(μ-dppa)Pt(PPh$_3$)]-[BF$_4$] (**4**): [Me$_3$O][BF$_4$] (118 mg, 0.8 mmol) was added to a solution of **2a** (557 mg, 0.5 mmol) in CH_2Cl_2 (15 ml). After stirring for 16 h, the yellow solution was concentrated to a volume of ca. 10 ml and then layered with Et_2O. After 2 d, yellow air-stable crystals were formed, which were suitable for analysis by X-ray crystallography. Yield: 465 mg (74%). – IR (KBr): $\tilde{\nu}$ = 3217 cm^{-1} (w) ν(NH); 2028 (m), 1961 (vs) ν(CO); 1542 (w) ν(CN). – ^{1}H NMR: δ = 2.24 (s, 6 H, xylyl-CH_3), 2.83 (s, 3 H, NMe), 6.38 [m, br., NH, ^{3}J(Pt–H) = 91 Hz], 6.96–7.62 (m, 38 H, phenyl). – ^{13}C{^{1}H} NMR: δ = 311.7 [ddd, μ-C, ^{2}J(P–C) = 82, ^{2}J(P–C) = 11, ^{2}J(P–C) = 3 Hz], 209.3 [dd, 2 CO, ^{2}J(P–C) = 27, ^{3}J(P–C) = 5 Hz], 208.5 [d, 1 CO, ^{2}J(P–C) = 7 Hz], 117.9–138.4 (m, phenyl), 51.6 [dt, N–CH_3, ^{4}J(P–C) = 9, ^{4}J(P–C) = 3 Hz], 17.1 (s, xylyl-CH_3). – ^{31}P{^{1}H} NMR: δ = 102.6 [dd, P1(Fe), ^{2+3}J(P1–P2) = 110, ^{3+4}J(P1–P3) = 11, ^{2+3}J(P1–Pt) = 70 Hz], 81.1 [dd, P2(Pt), ^{2}J(P2–P3) = 8, ^{1}J(P2–Pt) = 2837 Hz], 37.2 [dd, P3(Pt), ^{1}J(P3–Pt) = 3810 Hz]. – ^{195}Pt{^{1}H} NMR: δ = −2717 [ddd, ^{2+3}J(P1–Pt) = 70, ^{1}J(P2–Pt) = 2837, ^{1}J(P3–Pt) = 3808 Hz]. – $C_{55}H_{48}BF_4FeN_2O_3P_3Pt \cdot 0.5\ CH_2Cl_2$ (1215.66 + 42.47): calcd. C 52.98, H 3.93, N 2.23; found C 52.55, H 4.05, N 2.20.

Preparation of [(CO)$_3$Fe{μ-CN(Me)xylyl}(μ-Ph$_2$PNPPh$_2$)Pt-(PPh$_3$)] (**5**): KOSiMe$_3$ (3 mmol) was added to a suspension of **4** (0.5 mmol) in Et_2O (25 ml). The deprotonated product gradually dissolved within a period of 1 h. The yellow solution was then filtered and concentrated under reduced pressure. After addition of hexane, analytically pure **5** was precipitated. The product was filtered off and was dried in vacuo for 2 h. Yield: (447 mg, 84%). Suitable crystals for analysis by X-ray crystallography were obtained by layering a concentrated solution of **5** in CH_2Cl_2 with hexane. – IR (KBr): $\tilde{\nu}$ = ν(CO) 2002 cm^{-1} (m), 1934 (vs) ν(CO); ν(CN) 1538 (w) ν(CN). – ^{1}H NMR: δ = 2.22 (s, 6 H, xylyl-CH_3), 2.67 (s, 3 H, NMe), 7.01–7.85 (m, 38 H, phenyl). – ^{13}C{^{1}H} NMR: δ = 312.0 [dd, *μ*-C, ^{2}J(P–C) = 80, ^{2}J(P–C) = 19 Hz], 209.8 [dd, 2 CO, ^{2}J(P–C) = 27, ^{3}J(P–C) = 6 Hz], 208.6 [d, 1 CO, ^{2}J(P–C) = 8 Hz], 117.9–150.2 (m, phenyl), 51.4 [dt, N–CH_3, ^{4}J(P–C) = 9, ^{4}J(P–C) = 4 Hz], 17.4 (s, xylyl-CH_3). – ^{31}P{^{1}H} NMR: δ = 88.0 [br. d, P1(Fe), ^{2+3}J(P1–P2) = 130 Hz], 72.3 [br. d, P2(Pt), ^{1}J(P2–Pt) = 2554 Hz], 35.3 [d, P3(Pt), ^{2}J(P2–P3) = 12, ^{1}J(P3–Pt) = 3757 Hz]. – ^{195}Pt{^{1}H} NMR: δ = −2504 [br. dd, ^{1}J(P2–Pt) = 2554, ^{1}J(P3–Pt) = 3757 Hz]. – $C_{55}H_{47}FeN_2O_3P_3Pt$ (1127.85): calcd. C 58.57, H 4.20, N 2.48; found C 58.25, H 4.05, N, 2.10.

Crystal-Structure Determination of **3b**[14][15]: Collection of crystallographic data: Siemens Stoe AED 2 diffractometer; Mo-K_α radiation (λ = 0.71073 Å), graphite monochromator; intensity data were collected using the Ω/2Θ scan mode at 293 K. $C_{54}H_{44}F_3N_2FeO_7P_3PtS$: yellow crystals with approximate dimensions of 0.5 × 0.3 × 0.2 mm, triclinic, space group $P\bar{1}$; a = 13.105(3), b = 14.387(3), c = 14.997(7) Å, α = 81.29(3), β = 71.77(3), γ = 78.09(3)°, V = 2616.3(10) Å^3, Z = 2, ρ_{calcd} = 1.607 g cm^{-3}, F(000) = 1260; 9608 independent reflections in the scan range 2.38 < 2θ < 52.0°, of which 8455 with $I > 2\sigma(I)$ were used in the structure solution and refinement for 654 parameters; $R1 = \Sigma F_o - _{Fc} / \Sigma F_o$ = 0.0411[$I > 2\sigma(I)$], $wR2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2 / \Sigma wF_o{}^4]^{1/2}$ = 0.1222 (all data), GoF = 1.114; anisotropic refinement for non-hydrogen atoms; hydrogen atoms in idealized geometries, except for H(2), which was refined isotropically. Highest residual electron density 0.793 eÅ^{-3}.

Crystal Structure Determination of **5**: Collection of crystallographic data: Siemens Stoe AED 2 diffractometer; Mo-K_α radiation (λ = 0.71073 Å), graphite monochromator; intensity data were collected using the Ω/2Θ scan mode at 293 K. $C_{55}H_{47}FeN_2O_3P_3Pt$: yellow crystals with approximate dimensions of 0.65 × 0.4 × 0.35 mm, monoclinic, space group $P2_1/c$; a = 11.026(6), b = 18.524(9), c = 23.708(12) Å, β = 90.49(4)°, V = 4842.4(4) Å^3, Z = 4, ρ_{calcd} = 1.547 g cm^{-3}, F(000) = 2256; 7614 independent reflections in the scan range 1.72 < 2θ < 48.0°, of which 6095 with $I > 2\sigma(I)$ were used in the structure solution and refinement for 589 parameters; $R1 = \Sigma|F_o - F_c|/\Sigma|F_o|$ = 0.0295 [$I > 2\sigma(I)$], $wR2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma wF_o{}^4]^{1/2}$ = 0.0765 (all data), GoF = 1.036; anisotropic refinement for non-hydrogen atoms; hydrogen atoms in idealized geometries. Highest residual electron density 0.793 eÅ^{-3}.

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[15] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100733. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44(0)1223/336033; e-mail: teched@chemcrys.cam.ac.uk].

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