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Preliminary Communication

Synthesis of the heterodinuclear Fe-Pt complex [(OC)₃Fe{μ-CN(2,6-xylyl)}-(μ-dppm)Pt(PPh₃)] containing a bridging isonitrile ligand and electrophilic additions leading to μ-aminocarbyne complexes

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Abstract

Reaction of [(OC)₃{(MeO)₃Si}Fe(μ-dppm)PtH(PPh₃)] (1) (dppm = Ph₂PCH₂PPh₂) with 2,6-xylyl isonitrile (C≡NR) affords the heterodinuclear complex [(OC)₃Fe(μ-CNR)(μ-dppm)Pt(PPh₃)] (2) which contains a rare example of an isonitrile bridging a metal-metal bond. In the presence of HBF₄ or (Me₃O)BF₄, the bridging isonitrile is protonated or alkylated, leading to aminocarbyne (or iminium) type complexes [(OC)₃Fe(μ-CNRR′)(μ-dppm)Pt(PPh₃)][BF₄] (3, R′ = H, 4, R′ = Me). The synthesis of [(OC)₃Fe(η²-μ₂-Si(OMe)₂(OMe))(μ-dppm)Pt(CNR)][PF₆] (5) is also reported.

Homobinuclear complexes with bridging isonitrile of the type M(μ-CNR)M (both with bent or linear CNR groups) are a class of compounds similar to their well documented CO-bridged counterparts [1]. However, reports focussing on heterodinuclear complexes M(μ-CNR)M′ containing bridging isonitrile(s) appear to be still very scarce [2] and concern systems without metal–metal bond.

In the course of studies on dppm-bridged heterodinuclear silyl complexes of the type [(OC)₃{(MeO)₃Si}-Fe(μ-dppm)MLₙ] (dppm = Ph₂PCH₂PPh₂; M = Ni, Pd, Pt, Rh, Re, Ru,...) [3] we added dropwise at 0°C a CH₂Cl₂ solution of 2,6-xylyl isonitrile (0.132 g, 1 mmol) to a stirred suspension of [(OC)₃{(MeO)₃Si}Fe(μ-dppm)PtH(PPh₃)] (1) (1.048 g, 0.95 mmol) in CH₂Cl₂. The solution was stirred for 1 day at room temperature and then layered with Et₂O. After a few days at −10°C, orange air-stable crystals were isolated as dichloromethane solvate in 58% yield. The elemental

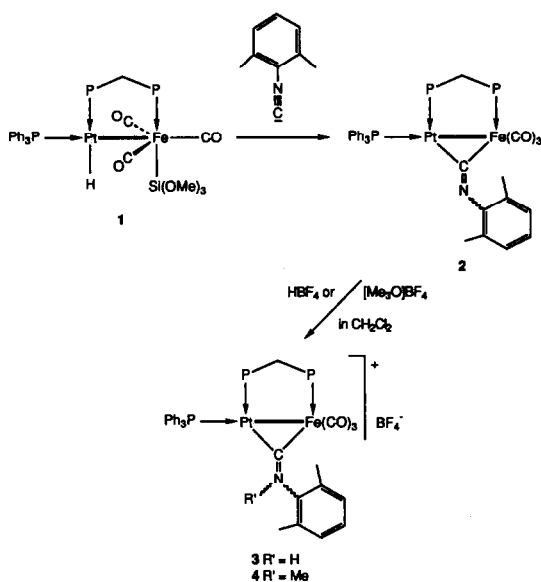analysis and spectroscopic data are consistent with the formulation [(OC)₃Fe(μ-CNR)(μ-dppm)Pt(PPh₃)] (2).

In addition to the ν(CO) vibrations at 1994(m) and 1926(vs, br), the IR spectrum of 2 contains a ν(CN) vibration at 1667(m, br) cm⁻¹. This low stretching frequency is indicative of a bridging, bent μ-RCN ligand [1g, 1k]. As a comparison, the complex [Pd₂Cl₂(μ-CNR)₂(py)₂] which contains two linear μ-RCN ligands has ν(CN) vibrations at 2056 and 1976 cm⁻¹ [1g]. In the ³¹P{¹H} NMR spectrum three mutually coupled phosphorus nuclei are observed, with a strong coupling of 152 Hz between the two P nuclei of the dppm and a weak cis coupling with the PPh₃ attached to Pt. The observation of a $^{2+3}J(P_{Fe}Pt)$ of 75 Hz [4*] supports the presence of a metal-metal bond [5], as exists in the precursor complex 1 [3a].

Two isomeric forms are conceivable due to the bent nature of the CNR group [1i]. The isomer with the bulkier xylyl group oriented toward the Fe centre would seem to be favoured on steric grounds, but we have no direct proof for this. The reaction may be initiated by insertion of the isonitrile in the Pt–H bond of 1, resulting in a formimidoyl intermediate [6] or, alternatively, by insertion into the M–SiR₃ bond [7] (intermediate species are observed during IR-monitoring of the reaction). A reductive elimination reaction of HSi(OMe)₃, similar to that observed in the reaction of the dinuclear Fe–Rh complex [(OC)₂Fe{η²-μ₂-Si-(OMe)₂(OMe)}(μ-dppm)(μ-H)RhCl] with CO [3d], can be ruled out since we found no evidence for ν(SiH) in the IR spectrum of the reaction mixture.

It is known that dinuclear complexes in which an isonitrile ligand bridges between two iron or two platinum centres are susceptible to protonation or alkylation at the nitrogen atom, due to its basic character, to give μ-iminium- or aminocarbyne-type derivatives [1k, 1n, 8]. In an analogous manner, 2 reacts instantly in cold CH₂Cl₂ with an excess of HBF₄ · Et₂O to give quantitative yields of [(OC)₃Fe{μ-CNH(R)}(μ-dppm)Pt(PPh₃)][BF₄] (3). Similarly, the nitrogen atom can be methylated by [Me₃O][BF₄] to give [(OC)₃-Fe{μ-CNMe(R)}(μ-dppm)Pt(PPh₃)][BF₄] (4) [4*]. The much lower ν[C=N(R)R′] frequencies in 3 (1527 cm⁻¹)

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* Reference number with asterisk indicates a note in the list of references.

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1

HBF₄ or / [Me₃O]BF₄

in CH₂Cl₂

2

3 R' = H
4 R' = Me

The Fe-Pt complex $[(OC)_3Fe\{\eta^2\text{-}\mu_2\text{-Si(OMe)}_2\text{-}(OMe)\}(\mu\text{-dppm})Pt(CNR)][PF_6]$ (5) containing a terminal isonitrile on platinum $[\nu(CN) = 2170 \text{ cm}^{-1}]$ was obtained in 80% yield by the reaction of the Fe-Pt bimetallic complex $[(OC)_3Fe\{\eta^2\text{-}\mu_2\text{-Si(OMe)}_2(OMe)\}(\mu\text{-dppm})PtCl]$ [3a] (0.675 g, 0.77 mmol) with 1 equivalent of CNR (0.102 g, 0.78 mmol) in cold CH_2Cl_2 in the presence of $TlPF_6$. The still rarely encountered $\eta^2\text{-}\mu_2$ alkoxysilyl bridge [3] in 5 is rigid in solution at ambient temperature, since the methoxy protons give rise to two distinct ^1H NMR resonances in the ratio 1:2 [4*].

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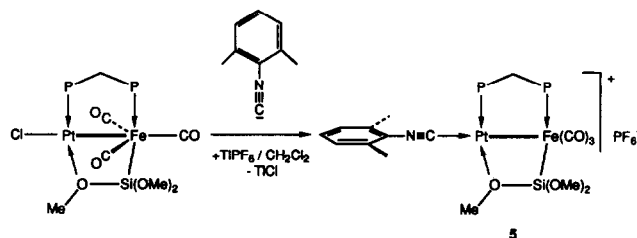
The factors which lead to elimination or retention of the silyl substituent in reactions of complexes of type 1 or 5 with isonitriles and the reactivity of 2 towards other electrophiles are currently under investigation.

and 4 (1550 cm⁻¹) when compared with $\nu(C=NR)$ in 2 (1667 cm⁻¹) point to the $\mu\text{-}[CN(R)R']^+$ group being an effective electron withdrawer and a much more powerful π-acceptor than μ-CNR. The frequencies are similar to the value of $\nu[C=NH(Me)]$ of 1525 cm⁻¹ in the structurally characterized aminocarbyne complex $[Ni_2\{\mu\text{-CNH(Me)}\}(CNMe)_2(\mu\text{-dppm})_2][PF_6]$ [1h]. Comparable values (1520 cm⁻¹ and 1553 cm⁻¹) were found in the mononuclear complexes $[W\{CNH(Me)\}(CNMe)(dppe)_2][BF_4]$ and $[W\{CNMe_2\}(CNMe)(dppe)_2][BF_4]$, respectively, which were also described as containing an aminocarbyne-like ligand [9]. The μ-CNRR' moieties in 3 and 4 may thus be viewed as bridging aminocarbynes (form A), although the contribution of the dimetallated iminium-type structure (form B) cannot be ignored. The latter description was preferred in $[Fe_2(\eta\text{-}C_5H_4Me)_2(\mu\text{-CO})(\mu\text{-C=NMe}_2)]I$ for which the $\nu[C=NMe_2]$ frequency was found at ca. 1600 cm⁻¹ [8c, 8f].

(A)
bridging aminocarbyne-like ligand

(B)
dimetalated iminium-like ligand

It is interesting to compare the reaction leading to 3 with the protonation by HBF_4 of $[(OC)_3Fe(\mu\text{-CO})(\mu\text{-dppm})Pt(PPh_3)]$, the carbonyl analogue of 2 [5]. In this case, protonation occurred at platinum to yield $[(OC)_4Fe(\mu\text{-dppm})Pt(H)(PPh_3)][BF_4]$, consistent with the higher inherent basicity of nitrogen compared to oxygen.

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4 Selected data: **2**: ^{1}H NMR (200 MHz, 28°C, CDCl$_3$, TMS as external reference): δ 2.18 (s, 6 H, CH$_3$), 3.69 (t, br, 2 H, PCH$_2$, ^2J(PH) 9.0 Hz, ^3J(PtH) 37 Hz), 6.83–7.49 (m, 38 H, aromatic). ^{31}P{^{1}H} NMR (81.02 MHz, 33°C, CH$_2$Cl$_2$/C$_6$D$_6$, H$_3$PO$_4$ as external reference): δ 32.7 (dd, P(Pt), ^{2+3}J(PP) = 152 Hz, ^2J(PP) = 27 Hz, ^1J(PPt) = 2527 Hz), 42.0 (dd, PPh$_3$(Pt), ^2J(PP) = 27 Hz, ^3J(PP) = 5 Hz, ^1J(PPt) = 4266 Hz), 73.6 (dd, P(Fe), ^{2+3}J(PP) = 152 Hz, ^3J(PP) = 5 Hz, ^2J(PPt) = 75 Hz). Anal. Found: C, 55.70; H, 4.18; N, 1.14. C$_{55}$H$_{46}$FeNO$_3$P$_3$Pt·CH$_2$Cl$_2$ (M = 1197.7) calc.: C, 56.15; H, 4.04; N, 1.17%.

3: IR (CH$_2$Cl$_2$): ν(CO) 2036 s, 1981 vs, 1969 vs, ν(CN) 1527 m; ν(NH) (KBr) 3215 w, br cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 2.18 (s, 6 H, CH$_3$), 4.41 (t, br, 2 H, PCH$_2$, ^2J(PH) 10.0 Hz, ^3J(PtH) 39.4 Hz), 6.89–7.69 (m, 38 H, aromatic), 9.18 (m, br, 1 H, NH). ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$/C$_6$D$_6$): δ 20.3 (dd, P(Pt), ^{2+3}J(PP) = 89 Hz, ^2J(PP) = 4 Hz, ^1J(PPt) = 2600 Hz), 38.2 (dd, PPh$_3$(Pt), ^2J(PP) = 4 Hz, ^3J(PP) = 12 Hz, ^1J(PPt) = 3740 Hz), 60.6 (dd, P(Fe), ^{2+3}J(PP) = 89 Hz, ^3J(PP) = 12 Hz, ^2J(PPt) = 90 Hz). Anal. Found: C, 49.40; H, 3.99; N, 0.97. C$_{55}$H$_{47}$BF$_4$FeNO$_3$P$_3$Pt·2CH$_2$Cl$_2$ (M = 1370.5) calc.: C, 49.95; H, 4.08; N, 0.79%.

4: IR (CH$_2$Cl$_2$): ν(CO) 2030 s, 1978 vs, 1961 vs, ν(CN) 1550 m cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 2.34 (s, 6 H, CH$_3$), 2.89 (s, 3 H,

NCH$_3$), 4.15 (t br, 2 H, PCH$_2$, ^2J(PH) 10.0 Hz, ^3J(PtH) 40.1 Hz), 6.92–7.64 (m, 38 H, aromatic). Mass spectrum (FAB$^+$): 1127.6 (M$^+$, 100%).

5: IR (CH$_2$Cl$_2$): ν(CN) 2170 s, ν(CO) 2010 s, 1958 s, 1933 s cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.91 (s, 6 H, CH$_3$), 3.83 (s, 6 H, (MeO)$_2$Si), 4.18 (d, 3 H, MeOPt, ^4J(PH) = 1.6 Hz, ^3J(PtH) = 22 Hz), 4.33 (t, 2 H, PCH$_2$P, ^2J(PH) = 11.0 Hz, ^3J(PtH) = 67.6 Hz), 6.96–7.82 (m, 23 H, aromatic). ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$/CDCl$_3$): δ −143.5 (spt, PF$_6$, ^1J(PF) = 713 Hz), 4.8 (d, P(Pt), ^{2+3}J(PP) = 45 Hz, ^1J(PPt) = 4176 Hz), 46.7 (d, P(Fe), ^{2+3}J(PP) = 45 Hz, ^2J(PPt) = 41 Hz). Anal. Found: C, 40.75; H, 3.49; N, 1.20. C$_{40}$H$_{40}$F$_6$FeNO$_6$P$_3$PtSi·CH$_2$Cl$_2$ (M = 1199.6) calc.: C, 40.98; H, 3.52; N, 1.17%.

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