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Reactions of platinum triflate complexes with carbon monoxide and t-butyl isonitrile

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Abstract

The platinum triflate complexes $[Pt(SO_3CF_3)_2(P\text{–}P)]$ (P–P = dppm, dppe) are reduced in the presence of carbon monoxide in acetone solution to produce $[Pt_2(CO)_2(\mu\text{-dppm})_2]^{2+}$ or the novel $[Pt_2(CO)_2(dppe)_2]^{2+}$ cation, which contains an unsupported metal–metal bond. The reactions of $[M(SO_3CF_3)_2(dppe)]$ (M = Pd, Pt) or $[Pt(SO_3CF_3)_2(dppm)]$ with CN^tBu in acetone proceed by initial displacement of the triflate ligands by CN^tBu. In the dppm case, dimerization occurs to yield $[Pt_2(CN^tBu)_4(\mu\text{-dppm})_2]^{4+}$, whereas with dppe cleavage of one of the isonitrile ligands occurs to produce 2-methylpropene and $[Pt(CN)(CN^tBu)(dppe)]^+$. Cleavage of the isonitrile is promoted by addition of ethanol or aniline. In the presence of excess diethylamine, addition to one of the isonitriles in $[Pt(CN^tBu)_2(dppe)]^{2+}$ is proposed to occur to generate a carbene complex, which is subsequently deprotonated to yield $[Pt\{C(NEt_2)\text{–}N^tBu\}(CN^tBu)(dppe)]^{2+}$.

Key words: Platinum; Carbon monoxide; Triflate; Isocyanide; Diphosphine; Group 10

1. Introduction

Platinum and palladium compounds containing weakly bound ligands represent useful precursors to a range of complexes of these two metals. Many of these, such as the dichloro compounds $[PtCl_2(cod)]$ (cod = 1,5-cyclooctadiene) [1], $[PdCl_2(cod)]$ [2], and $[MCl_2(PhCN)_2]$ [3], and the organometallic complexes $[PtR_2(cod)]$ [1], $[PtClR(cod)]$ [1] and $[PdClMe(cod)]$ [4], react by displacement of the weakly bound neutral ligand(s). Fewer examples exist in which it is the anionic fragments that may be displaced to generate cationic complexes, although a number of cationic species containing weakly bound ligands have been employed as homogeneous catalytic precursors [5].

We have previously reported the preparation of the triflate complexes $[M(SO_3CF_3)_2(P\text{–}P)]$ (M = Pd, Pt; P–P = dppm, dppe, dppp) [6,7]. The crystal structure of the platinum–dppe complex reveals that it exists as $[Pt(H_2O)_2(dppe)][SO_3CF_3]_2$ in the solid state [6]. We have shown that the triflate complexes react with tertiary phosphines [7], acetonitrile, or coordinated iodide [6], and that the complexes are suitable precursors for the synthesis of cyclopentadienyl complexes [8]. Each of these involves displacement of the triflate ligands. In this paper we describe some reactions with carbon monoxide or t-butyl isonitrile that are less straightforward.

2. Results and discussion

In contrast to the corresponding substitution reactions with tertiary phosphines [7], when carbon monoxide was bubbled through a d_6-acetone solution of $[Pt(SO_3CF_3)_2(dppm)]$ the expected monomeric dicarbonyl product was not obtained. Instead the dimeric species $[Pt_2(CO)_2(\mu\text{-dppm})_2]^{2+}$ was formed (eqn. (1)), in which the platinum has been reduced to platinum(I). The metal–metal bonded product was identified by comparison of its $^{31}P\{^1H\}$ NMR spectrum with that reported in the literature [9]. The reaction of $[Pt(OCOCF_3)_2(dppm)]$ with CO (4 atm, 100°C) has also been reported to result in reduction of platinum, but in this case the trinuclear complex $[Pt_3(\mu_3\text{-CO})(\mu\text{-dppm})_3]^{2+}$ was formed [10]. Subjecting the triflate complex to higher pressures (up to 10 atm) of CO did not produce

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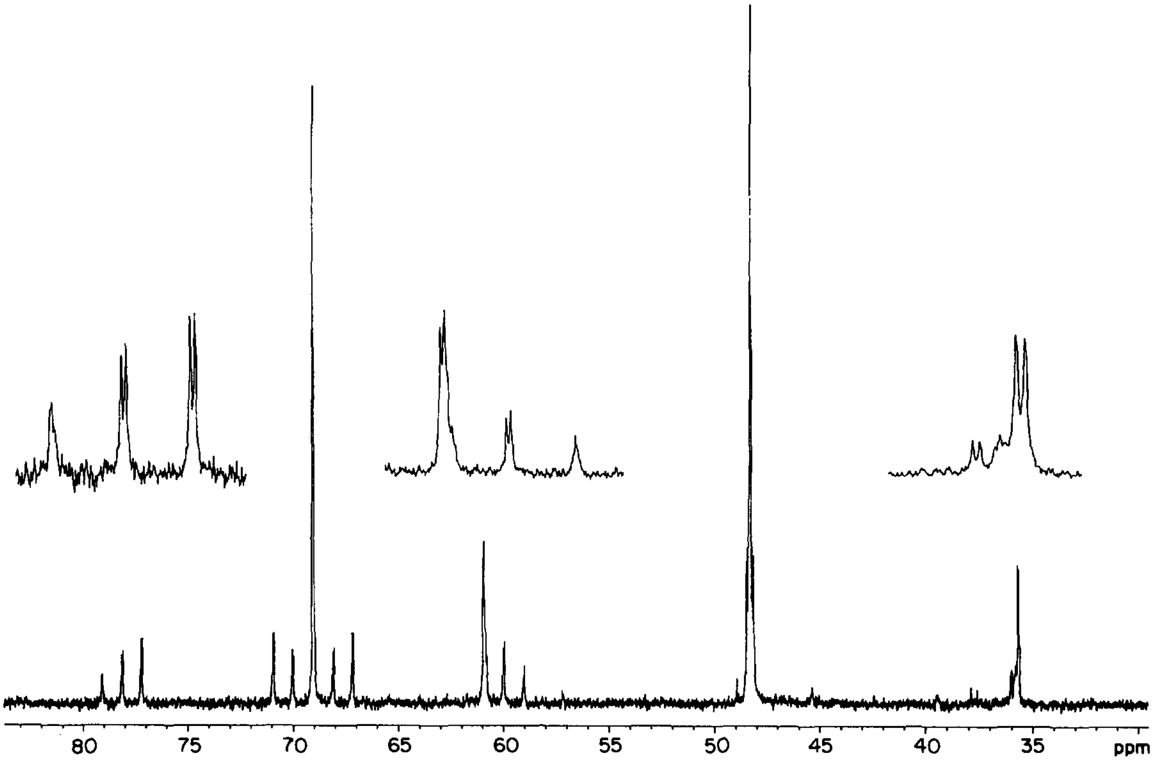


Fig. 1. $^{31}P\{^1H\}$ NMR spectrum of $[Pt_2(CO)_2(dppe)_2][SO_3CF_3]_2$ recorded in d_6-acetone solution.

the trimetallic species, however, and the dinuclear complex was formed in each case.

Many dimeric, dppm-bridged complexes of platinum are known, but it was somewhat surprising when the reaction of $[Pt(SO_3CF_3)_2(dppe)]$ with CO (1 atm) also produced a bimetallic species. In this case, however, the dppe ligands were chelating rather than bridging (eqn. (2)), as evidenced by the ^{31}P chemical shifts [11]. Its $^{31}P\{^1H\}$ NMR spectrum is shown in Fig. 1. The fact that there are two sets of ^{195}Pt satellites associated with each ^{31}P resonance is indicative of the dimeric nature of the complex (see Experimental details for

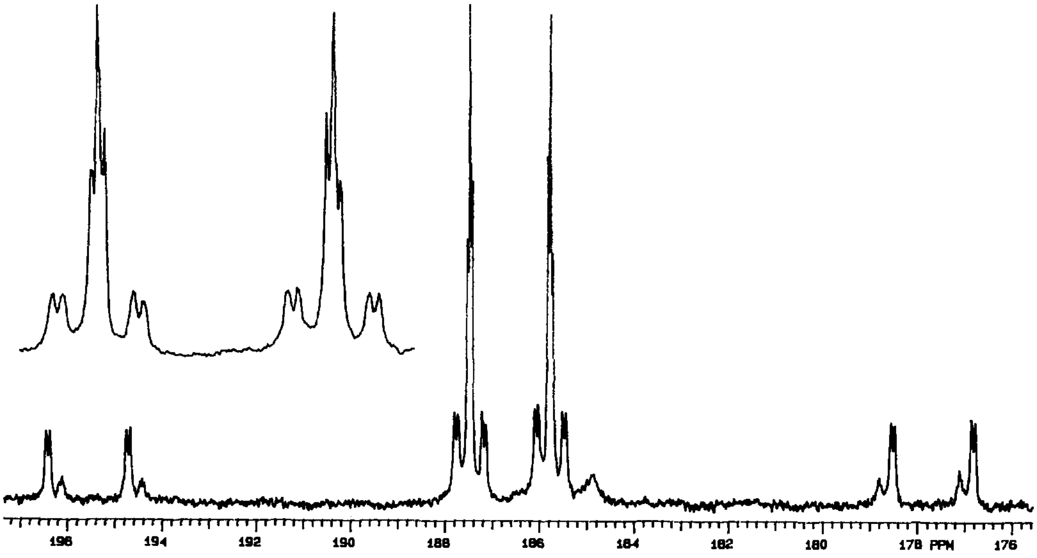
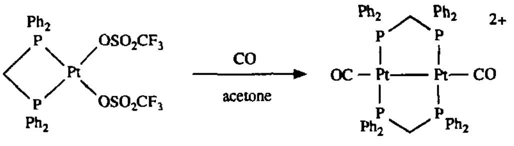


Fig. 2. $^{13}C\{^1H\}$ NMR spectrum of the carbonyl region for $[Pt_2(CO)_2(dppe)_2][SO_3CF_3]_2$ recorded in d_6-acetone solution.

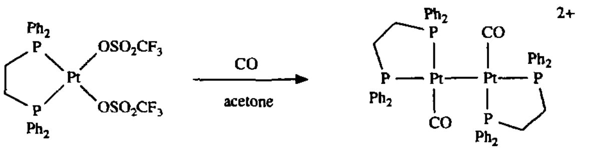


(1)

NMR parameters). The resonance at 70.0 ppm exhibits the one-bond and two-bond couplings to ^{195}Pt expected for a P atom lying *trans* to a Pt–Pt bond, although the ^{2}J(Pt, P) value is rather smaller than those found for terminal tertiary phosphines in cationic dppm-bridged platinum(I) complexes [12]. The couplings associated with the other resonance are consistent with a P atom located *trans* to a CO ligand and *cis* to a Pt–Pt bond. We were unable to isolate the complex in analytically pure form as its triflate salt, but metathesis with NH_4PF_6 allowed us to isolate it as its hexafluorophosphate salt.

In order to confirm the proposed geometry, the reaction was repeated using ^{13}CO, and the product was characterized spectroscopically. In the ^{31}P{^{1}H} NMR spectrum the resonance at 49.3 ppm was split into a doublet, with a ^{2}J(P,C) coupling constant of 128 Hz, confirming that this P atom lies *trans* to CO [13]. The ^{13}C{^{1}H} NMR spectrum is shown in Fig. 2. It consists of a doublet of triplets centered at δC 186.2, because of coupling with the *trans* phosphorus and with the two terminal P atoms. The central resonances are flanked by sets of signals because of short-range and long-range couplings to platinum. The weak ^{13}C resonances because of the ^{195}Pt$_2$ isotopomer lie inside the signals resulting from ^{1}J(Pt,C) associated with the isotopomer containing one ^{195}Pt, indicating that the one-bond and two-bond Pt–C couplings are of opposite sign [14]. In contrast, for the terminal P atoms, the ^{1}J(Pt, P) and ^{2}J(Pt, P) values are of the same sign.

Reactions of metal carbonyl and isonitrile complexes in the presence of water which result in reduction of the metal center have been shown to occur [15]. The platinum isonitrile complex $[Pt(CNMe)_4]^{2+}$, for example, is reduced by water to give the diplatinum species $[Pt_2(CNMe)_6]^{2+}$, and nucleophilic attack of H_2O at the coordinated isonitrile was thought to be responsible for the reduction [16]. Similarly, chromium, molybdenum and tungsten carbonyl complexes have been reduced by water *via* loss of CO_2 and H^+ to give species in which the oxidation state of the metal is reduced by two [17]. The reduction of $[Pt(CO)_2(P\text{–}P)]^{2+}$ (P–P = dppm, dppe) is presumably involved in the formation of $[Pt_2(CO)_2(\mu\text{-dppm})_2]^{2+}$ and $[Pt_2(CO)_2(dppe)_2]^{2+}$. A mechanism to account for the formation of the latter is shown in Scheme 1. A similar mechanism may be envisioned for the dppm complex.



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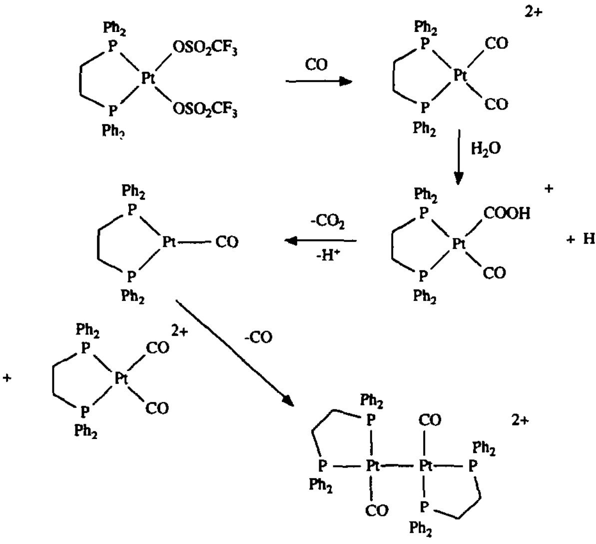


Scheme 1.

When $[Pt(SO_3CF_3)_2(dppm)]$ was treated with 2 mol equivalent of t-butyl isonitrile in d_6-acetone solution, broad signals consistent with the $[Pt(CN^tBu)_2(dppm)]^{2+}$ cation (δP −54.0, ^{1}J(Pt, P) = 2255 Hz) were observed. These disappeared over a period of 24 h, and were replaced by those resulting from $[Pt_2(CN^tBu)_4(\mu\text{-dppm})_2]^{4+}$ (δP 0.0, ^{1}J(Pt, P) = 2294 Hz, ^{2}J(Pt, P) = 56 Hz, ^{2}J(P, P) = 28 Hz and < 5 Hz) [18]. When the reaction was carried out in $CDCl_3$, conversion to the dppm-bridged species was much slower, a 1 : 1 mixture of the monomer and the dimer being present after six days at ambient temperature. Addition of a drop of water to the d_6-acetone solution greatly increased the rate of reaction of the monomeric species. The $[Pt_2(CN^tBu)_4(\mu\text{-dppm})_2]^{4+}$ cation has been prepared previously from $[PtCl_2(dppm)]$ and 2 mol equivalents of CN^{t}Bu, and was isolated as its PF_6^- salt [18]. In contrast to that earlier report, we find the $[Pt_2(CN^tBu)_4(\mu\text{-dppm})_2]^{4+}$ cation to be quite soluble as its triflate salt in $CDCl_3$ or acetone.

The bis(isonitrile) complex $[Pt(CN^tBu)_2(dppe)]^{2+}$ was formed in the reaction of the triflate complex with 2 mol equivalents of CN^{t}Bu. This complex was isolated in good yield, and it is indefinitely stable in dry solvents. The palladium analogue was also obtained, but it does not display the same degree of stability in solution.

Bimetallic species were not formed when $[\mathrm{Pt(CN^tBu)_2(dppe)}]^{2+}$ was allowed to react with water. Instead, dealkylation of one of the isonitrile ligands occurred. Monitoring the reaction by NMR spectroscopy allowed the observation of signals from 2-methylpropene (δH 1.68 t, $\mathrm{C(C}H_3)_2$, 4.62 septet, $=\mathrm{C}H_2$, ^4J(H, H) = 1.2 Hz), and the $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum was consistent with $[\mathrm{Pt(CN)(CN^tBu)(dppe)}]^+$ as the major product (δP 45.3 br d, ^1J(Pt, P) = 2740 Hz; δP 47.3 d, ^1J(Pt, P) = 2344 Hz, ^2J(P, P) = 9 Hz). The palladium analogue also reacted with water, but produced a number of unidentified phosphorus-containing products. 2-Methylpropene was again formed. Elimination of 2-methylpropene from coordinated t-butyl isonitrile has been reported previously in the reaction of $[\mathrm{Zr_2Cl_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_{10}H_8)(\mu\text{-}CN^tBu)}]$ with $\mathrm{CN^tBu}$ in the presence of Na/Hg [19].

When excess ethanol was added to a $\mathrm{C_6D_6}$ solution of $[\mathrm{Pt(CN^tBu)_2(dppe)}][\mathrm{SO_3CF_3}]_2$ the cyano complex was again formed. Similarly, treatment of the bis(isonitrile) cation with excess aniline in $\mathrm{CDCl_3}$ solution produced $[\mathrm{Pt(CN)(CN^tBu)(dppe)}]^+$. In each case the reaction was slow at ambient temperature. When the reaction with aniline was heated to 50°C, the ^{31}P signals associated with the cyano complex grew in more rapidly, but further reaction took place to give an unidentified species which exhibited a singlet resonance in its $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum (δP 42.2, ^1J(Pt, P) = 2476 Hz).

Treatment of $[\mathrm{Pt(CN^tBu)_2(dppe)}]^{2+}$ with 1 mol equivalent of diethylamine in $\mathrm{CDCl_3}$ solution produced a complex with non-equivalent P atoms (δP 39.9 d, ^1J(Pt, P) = 2643 Hz; δP 42.0 d, ^1J(Pt, P) = 1917 Hz, ^2J(P, P) = 8 Hz), which was gradually replaced by a second such species (δP 38.7 d, ^1J(Pt, P) = 2040 Hz; δP 39.1 d, ^1J(Pt, P) = 2643 Hz, ^2J(P, P) = 9 Hz). When excess $\mathrm{Et_2NH}$ was employed the first species was not observed. The products decomposed at rates comparable with their formation, so we have been unable to isolate these species. We suggest that the greater nucleophilicity of $\mathrm{Et_2NH}$, compared with water, ethanol or aniline, allows its attack on the coordinated isonitrile to compete favorably with the elimination of 2-methylpropene to form the cyano complex. We propose that the first step is $\mathrm{Et_2NH}$ addition to one of the coordinated $\mathrm{CN^tBu}$ ligands to give a carbene complex, which is followed by $\mathrm{H^+}$ abstraction by a second $\mathrm{Et_2NH}$ molecule (eqn. (3)). This accounts for the increased rate of the second step in the presence of excess diethylamine. Attack on neutral isonitrile complexes of platinum and palladium to form carbene species is well documented [20], and a cationic species should be even more susceptible to attack of this nature.

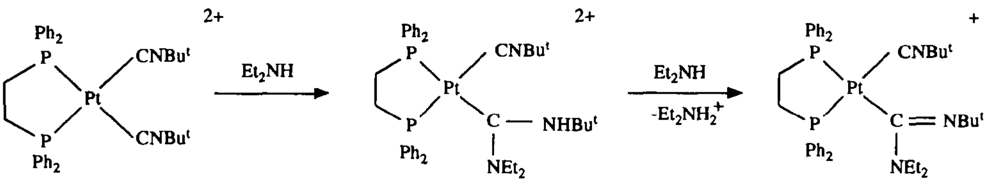
In summary, we have shown that reactions of platinum(II) triflate complexes with carbon monoxide lead to bimetallic complexes containing Pt–Pt bonds, in which the metal is reduced to platinum(I). A mechanism for this process, implicating the reduction of a dicarbonyl species by water, has been proposed. The bis(isonitrile) complexes $[\mathrm{Pt(CN^tBu)_2(P\text{–}P)}]^{2+}$ (P–P = dppm, dppe) were prepared, and these were shown to undergo dimerization in the case of dppm, or attack at the coordinated isonitrile in the case of dppe.

3. Experimental details

The triflate complexes were prepared as described previously [6,7]. t-Butyl isonitrile and carbon-13 monoxide (99%) were purchased from Aldrich. NMR spectra were recorded on a Varian XL-300 spectrometer. ^{1}H and ^{13}C NMR spectra were referenced to the residual solvent resonance, and ^{31}P NMR spectra were referenced to external $\mathrm{H_3PO_4}$, positive shifts representing deshielding.

3.1. Preparation of $[\mathrm{Pt_2(CO)_2(dppe)_2}][\mathrm{SO_3CF_3}]_2$

Carbon monoxide was bubbled through a solution of $[\mathrm{Pt(H_2O)_2(dppe)}][\mathrm{SO_3CF_3}]_2$ (0.151 g, 0.16 mmol) in acetone (150 mL) for 6 h. During this time the solution changed from colorless to green. The solution was evaporated to dryness, and the residue was extracted with $\mathrm{CH_2Cl_2}$ (25 mL). The $\mathrm{CH_2Cl_2}$ solution was filered, then concentrated, and ether addition gave the product as a pale green solid (0.053 g, 43%). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (d_6-acetone): $\delta\mathrm{P}_{1,4}$ 70.0, $^1J(\mathrm{Pt, P_1})$ =



(3)

^1J(Pt, P$_4$) = 2090 Hz, ^2J(Pt, P$_1$) = ^2J(Pt, P$_4$) = 344 Hz; δP$_{2,3}$ 49.3, ^1J(Pt, P$_2$) = ^1J(Pt, P$_3$) = 3065 Hz, ^2J(Pt, P$_2$) = ^2J(Pt, P$_3$) = 34 Hz; ^3J(P$_1$, P$_4$) 112 Hz, ^3J(P$_1$, P$_3$) = ^3J(P$_2$, P$_4$) = 8 Hz, ^3J(P$_2$, P$_3$) = 0 Hz. ^{13}C{^{1}H} NMR (d_6-acetone): δC 186.2, ^1J(Pt, C = 1352 Hz, ^2J(Pt, C) = 44 Hz, ^2J(P$_2$, C) = ^2J(P$_3$, C) = 128 Hz, ^2J(P$_1$, C) = ^2J(P$_4$, C) = 4 Hz, ^3J(C, C) = 6 Hz. Replacement of the triflate anions by hexafluorophosphate using NH_4PF_6 allowed the complex to be isolated in pure form. Calc. for $C_{54}H_{48}F_{12}O_2P_6Pt_2$: C, 42.3; H, 3.2. Found: C, 42.1; H, 3.1%.

3.2. *Reaction of [Pd(H$_2$O)$_2$(dppe)][SO$_3$CF$_3$]$_2$ with CO*

This resulted in decomposition, the only species detected in solution during the reaction being the starting complex.

3.3. *Reaction of [Pt(SO$_3$CF$_3$)$_2$(dppm)] with CO*

Carbon monoxide was bubbled for 1 h into a d_6-acetone solution (0.5 mL) of [Pt(SO$_3$CF$_3$)$_2$(dppm) (*ca.* 15 mg) in a NMR tube. After this time the only species detected in solution was the [Pt$_2$(CO)$_2$(μ-dppm)$_2$]$^{2+}$ cation (δP −5.0, ^1J(Pt, P) = 2390 Hz, ^2J(Pt, P) = 96 Hz, J(P, P) = 46 and 33 Hz). A similar result was obtained when the reaction was performed in a stainless steel autoclave and a CO pressure of 10 atm was employed.

3.4. *Preparation of [Pt(CN^{t}Bu)$_2$(dppe)][SO$_3$CF$_3$]$_2$*

To a CH_2Cl_2 solution of [Pt(H$_2$O)$_2$(dppe)][SO$_3$CF$_3$]$_2$ (0.21 g, 0.23 mmol) was added CN^{t}Bu (62 μL, 0.55 mmol). After 1 h the solution was concentrated and ether was added to precipitate the product as a fluffy, white solid, which was washed with ether and dried (0.22 g, 89%). Anal. Calc. for $C_{38}H_{42}F_6N_2O_6P_2PtS_2$: C, 43.1; H, 4.0. Found: C, 43.0; H, 4.0%. ^{31}P{^{1}H} NMR: δP 45.2, ^1J(Pt, P) = 2628 Hz (in CDCl$_3$); δP 48.1, ^1J(Pt, P) = 2618 Hz (in $d_6$acetone). ^{1}H NMR: δH 1.31 s, C(C*H*$_3$)$_3$; 2.85–3.05 m, C*H*$_2$; 7.6 m, 7.8 m, C$_6$*H*$_5$ (in CDCl$_3$); δH 1.40 s, C(C*H*$_3$)$_3$; 3.14–3.34 m, C*H*$_2$; 7.7 m, 8.0 m, C$_6$*H*$_5$ (in d_6-acetone). ^{13}C{^{1}H} NMR (CDCl$_3$): δC 28.9 s, C(*C*H$_3$)$_3$; 28.9 dd, J(P, C) = 70 and 5 Hz, *C*H$_2$; 61.0 s, *C*(CH$_3$)$_3$; 124.2 d (64), 130.3 t (6), 133.5 t (6), 133.7 s, *C*$_6$H$_5$; *C*N not observed. The [Pt(CN^{t}Bu)$_2$(dppe)]$^{2+}$ cation was also generated by addition of 2 mol equivalents of CN^{t}Bu to a CD_2Cl_2 solution of [Pt(cod)(dppe)][ClO$_4$]$_2$.

3.5. *Preparation of [Pd(CN^{t}Bu)$_2$(dppe)][SO$_3$CF$_3$]$_2$*

This complex was prepared similarly. Anal. Calc. for $C_{38}H_{42}F_6N_2O_6P_2PdS_2$: C, 47.1; H, 4.4. Found: C, 47.1; H, 4.3%. ^{31}P{^{1}H} NMR: δP 66.0 (in CDCl$_3$); δP 69.3 (in d_6-acetone). ^{1}H NMR (in CDCl$_3$): δH 1.29 s, C(C*H*$_3$)$_3$; 2.91–3.11 m, C*H*$_2$; 7.6 m, 7.8 m, C$_6$*H*$_5$. ^{13}C{^{1}H} NMR: δC 29.0 s, C(*C*H$_3$)$_3$; 29.2 dd, J(P,C) = 35 and 11 Hz, *C*H$_2$; 60.2 s, *C*(CH$_3$)$_3$; 125.5 d (56), 130.1 d (12), 133.3 d (12), 133.5 d (3), *C*$_6$H$_5$; *C*N not observed.

3.6. *Reaction of [Pt(SO$_3$CF$_3$)$_2$(dppm)] with CN^{t}Bu*

(a) To a suspension of [Pt(SO$_3$CF$_3$)$_2$(dppm)] (*ca.* 15 mg) in CDCl$_3$ (0.5 mL) was added CN^{t}Bu (2 mol equiv). The mixture was shaken and the ^{31}P{^{1}H} NMR spectrum indicated the presence of the [Pt(CN^{t}Bu)$_2$(dppm)]$^{2+}$ cation (δP −54.1, ^1J(Pt, P) = 2264 Hz).

(b) To a solution of [Pt(SO$_3$CF$_3$)$_2$(dppm)] (*ca.* 15 mg) in d_6-acetone (0.5 mL) was added 2 mol equiv of CN^{t}Bu and the ^{31}P{^{1}H} NMR spectrum was recorded immediately (δP −54.0, ^1J(Pt, P) = 2255 Hz). After standing at ambient temperature for 24 h quantitative conversion to the [Pt$_2$(CN^{t}Bu)$_4$(μ-dppm)$_2$]$^{4+}$ cation took place (δP 0.0, ^1J(Pt, P) = 2294 Hz, ^2J(Pt, P) = 56 Hz, J(P, P) = 28 and < 5 Hz).

3.7. *Reaction of [Pt(CN^{t}Bu)$_2$(dppe)][SO$_3$CF$_3$]$_2$ with moist acetone*

A d_6-acetone solution (0.5 mL) of [Pt(CN^{t}Bu)$_2$(dppe)][SO$_3$CF$_3$]$_2$ (*ca.* 20 mg) was monitored by NMR spectroscopy over several days. The initial complex was slowly converted to a second species (δP 47.3 d, ^1J(Pt, P) = 2344 Hz; δP 45.3 d, ^1J(Pt, P) = 2740 Hz, ^2J(P, P) = 8 Hz; δH 1.68 d, 4.62 septet, J(H, H) = 1.2 Hz).

3.8. *Reaction of [Pt(CN^{t}Bu)$_2$(dppe)][SO$_3$CF$_3$]$_2$ with PhNH$_2$*

A CDCl$_3$ solution (0.5 mL) of [Pt(CN^{t}Bu)$_2$(dppe)][SO$_3$CF$_3$]$_2$ (*ca.* 15 mg) was treated with aniline (0.05 mL). Heating to 50°C for 6 h caused conversion to a mixture of two species (δP 43.8 d, ^1J(Pt, P) = 2722 Hz; δP 45.6 d, ^1J(Pt, P) = 2345 Hz, ^2J(P, P) = 8 Hz, and δP 42.2, ^1J(Pt, P) = 2476 Hz). Further heating resulted in the disappearance of the doublet resonances, but significant decomposition occurred also.

3.9. *Reaction of [Pt(CN^{t}Bu)$_2$(dppe)][SO$_3$CF$_3$]$_2$ with EtOH*

In a manner similar to that described above, [Pt(CN^{t}Bu)$_2$(dppe)][SO$_3$CF$_3$]$_2$ was treated with ethanol (20 μL) in C_6D_6 solution. After standing for 24 h approximately 80% of the starting material remained, but a new species had begun to form (δP 45.6 d, ^1J(Pt, P) = 2355 Hz; δP 43.8 d, ^1J(Pt, P) = 2723 Hz, ^2J(P, P) = 7 Hz). Decomposition took place before this new species was produced to a significant extent.

3.10. Reaction of $[Pt(CN^tBu)_2(dppe)][SO_3CF_3]_2$ *with* Et_2NH

A $CDCl_3$ solution (0.5 mL) of $[Pt(CN^tBu)_2(dppe)][SO_3CF_3]_2$ (*ca.* 20 mg) was treated with diethylamine (20 μL). After 1 h a new species was observed by $^{31}P\{^1H\}$ NMR spectroscopy (δP 42.0 d, $^1J(Pt, P) = 1916$ Hz; δP 39.9 d, $^1J(Pt, P) = 2948$ Hz, $^2J(P, P) = 8$ Hz). After standing for a further 1 h another species had begun to form (δP 39.0 d, $^1J(Pt, P) = 2643$ Hz; δP 38.7 d, $^1J(Pt, P) = 2040$ Hz, $^2J(P, P) = 9$ Hz), but decomposition occurred before this species was formed in a significant quantity.

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