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XYLYL ISOCYANIDE PLATINUM AND PALLADIUM COMPLEXES

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Summary

Bis(cycloocta-1,5-diene)platinum reacts with isopropyl isocyanide to give the trinuclear complex $[Pt_3(CNPr^i)_6]$. A related palladium compound was prepared by treating either $[Pd(dba)_2]$ or $[Pd_2(dba)_3CHCl_3]$ with 2,6-dimethylphenyl isocyanide. Reactions of the cluster $[Pt_3(CNC_6H_3\text{-}2,6\text{-}Me_2)_6]$ and its presumed palladium analogue with the olefins $(NC)_2C{:}C(CN)_2$, $F_2C{:}CFCl$ and $(CN)_2C{:}C(CF_3)_2$, give the compounds $[M(olefin)(CNC_6H_3\text{-}2,6\text{-}Me_2)_2]$ (M = Pt, Pd) in which the metals are η^2-bonded to the coordinated olefins. The compound $[Pd_3(CNC_6H_3\text{-}2,6\text{-}Me_2)_6]$ reacts with $F_2C{:}CFBr$ and with $F_2C{:}CFCl$ to give the *trans* complexes $[Pd(X)(C_2F_3)(CNC_6H_3\text{-}2,6\text{-}Me_2)_2]$ (X = Br, Cl). Similar compounds $[M(L)(CNC_6H_3\text{-}2,6\text{-}Me_2)_2]$ (M = Pt, Pd), (L = $MeO_2CHC{:}CHCO_2Me$, $OOCH{:}CHCOO$) have also been prepared, and characterised. Two platinum complexes $[\{Pt(CH{:}NC_6H_3\text{-}2,6\text{-}Me_2)(SiMePh_2)(CNC_6H_3\text{-}2,6\text{-}Me_2)\}_2]$ and $[Pt_2\{\mu\text{-}(PhC)_2CO\}(CNC_6H_3\text{-}2,6\text{-}Me_2)_4]$ have been synthesized by treating the complex $[Pt_3(CNC_6H_3\text{-}2,6\text{-}Me_2)_6]$ with $HSiMePh_2$ and cyclopropenone, respectively. NMR and IR data for the new species are reported and discussed.

Introduction

The development of a practical synthesis of $[Pt(cod)_2]$ (cod = cycloocta-1,5-diene) [1] provided a route to platinum isocyanide complexes by displacement of the diene ligands with isocyanides [2], and so far reactions of $[Pt(cod)_2]$ with CNR (R = Me, Et, Bu^t, cyclo-C_6H_{11}) have been reported, the products being the triplatinum species $[Pt_3(\mu\text{-}CNR)_3(CNR)_3]$. In order to extend previous work we now report the synthesis and some reactions of the species $[M_3(\mu\text{-}CNC_6H_3\text{-}2,3\text{-}Me_2)_3(CNC_6H_3\text{-}2,3\text{-}Me_2)_3]$ (M = Pd or Pt). The structures of these complexes are given in Scheme 1.

An X-ray diffraction study [2] revealed that in $[Pt_3(\mu\text{-}CNBu^t)_3(CNBu^t)_3]$ the platinum atoms form an approximately equilateral triangle and carry both terminal and bridging isocyanide groups. It was thought that 2,6-dimethylphenyl isocyanide might react with $[Pt(cod)_2]$ differently than the previously studied isocyanides. However, the product of this reaction turned out to have a structure identical with

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that of the t-butyl isocyanide analogue, as shown by the IR and NMR spectra [3].

As far as palladium is concerned, some years ago, Malatesta [4,5] and Fischer et al. [6] reported several palladium complexes which they formulated as $[Pd(CNR)_2]$, but the nature of these species was not clearly understood. Some similar species $[M(CNBu^t)_2]$ (M = Ni or Pd) were also prepared by Japanese workers, [7] and shown to be air sensitive, in contrast to $[Pt_3(CNBu^t)_6]$, which is relatively inert to air. The existence of a palladium analogue of $[Pt_3(CNR)_6]$ has not been conclusively demonstrated, although Thomas et al. [8] have claimed that the product of the reaction of $[Pd(\eta^3\text{-}C_3H_5)(\eta\text{-}C_5H_5)]$ with Bu^tNC is a trimer.

The complex $[Pt_3(CNBu^t)_6]$ reacts with hexakis(trifluoromethyl)benzene and with diphenylcyclopropenone with carbon–carbon bond cleavage [9,10,11]. The same, triplatinum species reacts with chlorotrifluoroethylene affording a three-membered ring complex which undergoes a vinyl rearrangement to give the complex *trans*-$[Pt(Cl)(C_2F_3)(CNBu^t)_2]$ [12]. In contrast, the same substrate reacting with $[Pd(CNBu^t)_2]$ forms directly the trifluorovinyl η^1 species [13].

Hexafluoropropene and 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene also give three-membered ring compounds with $[Pd(CNBu^t)_2]$ [13]. Reactions of $[Pt_3(CNBu^t)_6]$ with olefins carrying electronegative substituents e.g. dimethyl or diethyl fumarate, maleic anhydride, or dimethyl maleate produce complexes of the type $[Pt(olefin)(CNBu^t)_2]$ [14]. All the above mentioned reactions demonstrate clearly that the triplatinum isocyanide complexes form compounds containing the fragment $[Pt(CNR_2)]$.

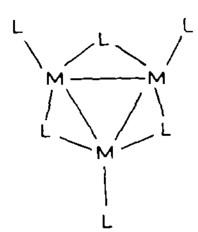
Triorganosilanes add oxidatively to $[Pt_3(CNBu^t)_6]$ to give a family of products [15]. The spectroscopic properties of these compounds can be accounted for in terms of six-membered ring structures. A single-crystal X-ray study of the compound $[\{Pt(CH{:}NCBu^t)(SiMePh_2)(CNBu^t)\}_2]$ established a central diplatina-ring structure, the six-membered ring being of boat conformation [15].

Results and discussion

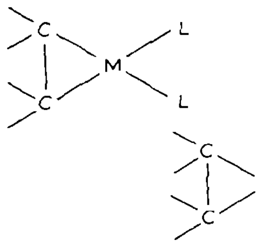
Addition of an excess of $CNPr^i$ to a suspension of $[Pt(cod)_2]$ in hexane gave a red crystalline complex (I) in high yield. The ^1H NMR spectrum of I shows two doublets at τ 8.48 and 8.68 ppm, corresponding to bridging and terminal isopropyl groups, respectively. The ^{13}C NMR spectrum exhibits two broad peaks at δ 22.9 and 21.3 ppm ascribable to $CHMe_2$ and to the Me substituents of the isopropyl groups, respectively. The fact that there are two such peaks and that these are broad indicates dynamic behaviour similar to that observed for the complex $[Pt_3(CNBu^t)_6]$ [2].

By treating either $[Pd(dba)_2]$ or $[Pd_2(dba)_3 \cdot CHCl_3]$ (dba = dibenzylideneacetone) with an excess of xylyl isocyanide (xylyl = 2,6-dimethylphenyl) in hexane, a yellow precipitate was formed, which on addition of diethyl ether afforded a deep red solid, which appears to be the tripalladium compound II. This complex II is assigned a structure analogous to that of $[Pt_3(CNBu^t)_6]$ on the basis of the elemental analysis and ^1H NMR spectrum. Moreover, the reactivity pattern corresponds to that of compound II, acting as formal source of 14-electron species $[Pd(CNC_6H_3\text{-}2,6\text{-}Me_2)_2]$.

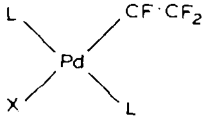
The ^1H NMR spectrum at −90°C is not sufficiently clear to permit relevant conclusions. Because of the great sensitivity of its solutions to air it has been



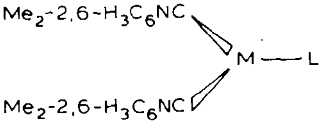
(I, M = Pt; L = CNPr^i,
II, M = Pd; L = CNC_6H_3-2,6-Me_2)



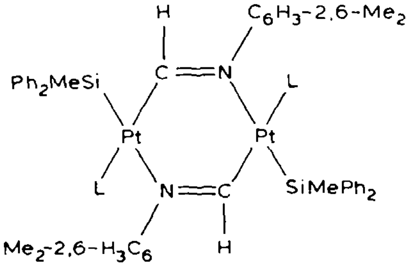
	L	M	
III	CNC_6H_3-2,6-Me_2	Pt	$F_2C:CFCl$
IV	CNC_6H_3-2,6-Me_2	Pt	$(CN)_2C:C(CF_3)_2$
V	CNC_6H_3-2,6-Me_2	Pd	$(CN)_2C:C(CF_3)_2$
VI	CNC_6H_3-2,6-Me_2	Pt	$(NC)_2C:C(CN)_2$



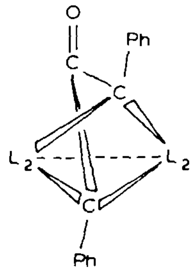
(VII, X = Cl; L = CNC_6H_3-2,6-Me_2;
VIII, X = Br; L = CNC_6H_3-2,6-Me_2)



	M	L
IX	Pt	$MeO_2CHC:CHCO_2Me$
X	Pd	$MeO_2CHC:CHCO_2Me$
XI	Pt	$\overline{OCOHC:CHOC}$
XII	Pd	$\overline{OCOHC:CHOC}$



(XIII, L = CNC_6H_3-2,6-Me_2)



(XIV, L = CNC_6H_3-2,6-Me_2)

SCHEME I

impossible to grow suitable crystals of the compound II for X-ray studies. Molecular weight measurements in degassed $CHCl_3$ gave a value of 502, which is almost half of the expected molecular weight (1,106) for the tripalladium complex II.

Complex III is formed from the reaction between chlorotrifluoroethylene and the compound $[Pt_3(CNC_6H_3\text{-}2,6\text{-}Me_2]$. The ^{19}F NMR spectrum (Table 2) shows that III contains a three-membered metallacyclopropane ring. The chemical shifts of the ^{19}F as well as the ^{195}Pt coupling being almost the same as for the t-butyl isocyanide analogue [12]. The ^1H NMR spectrum of compound III shows a doublet at τ 7.54 ppm assignable to the methyl groups of two different isocyanide ligands. The formulation of III as an η^2-complex also follows from the absence from the IR spectrum (see Experimental) of any band near 1700 cm^{-1} due to the $CF:CF_2$ group [16]. However, solutions of compound III in acetone undergo a vinyl rearrangement after standing for a week. The IR spectrum of the solid remaining after the removal of volatile material showed a strong peak at 1706 cm^{-1}, indicating the presence of a $CF:CF_2$ group [16]. Moreover, the ^{19}F NMR spectrum in $CDCl_3$ taken after 4 h had peaks assignable to both the three-membered ring (or η^2-structure) and a trifluorovinyl group.

Excess of the olefin $(CF_3)_2C:C(CN)_2$ reacts with $[Pt_3(CNC_6H_3\text{-}2,6\text{-}Me_2)_6]$ and with II in diethyl ether at room temperature to give complexes IV and V, respectively. The ^{19}F NMR spectra of these complexes show a singlet at ca. 55 ppm, having platinum satellites (Table 2). This is the usual ^{19}F NMR spectral pattern for platinum complexes of $(CN)_2C:C(CF_3)_2$ [12,13,17,18,19,20].

The ^1H NMR spectra of both compounds (Table 3) show two peaks at ca. τ 7.50 ppm, indicating slightly different environments for the two isocyanide ligands, the spectrum being similar to that of the complex $[\{\overline{PtC(CF_3)_2\cdot C}(CN)_2\}(Bu^tNC)_2]$, which shows two peaks at ca. τ 8.40 ppm. The IR spectra of the complex IV and V show two bands in the ν(NC) region, in accord with a *cis*-$(RNC)_2Pt$ group.

Treatment of $[Pt_3(CNC_6H_3\text{-}2,6\text{-}Me_2)_6]$ with TCNE in diethyl ether at room temperature gave the complex VI in good yield (Table 1). The ^1H NMR spectrum shows a singlet at τ 7.49 ppm again indicating two equivalent isocyanide ligands. The ^{13}C NMR spectrum of VI exhibits a reasonance at 113.3 ppm with J(PtC) 49 Hz, which may be assigned to the cyano carbon atom. Surprisingly, reaction between TCNE and $[Pt_3(CNBu^t)_6]$ does not give an analogous product, but instead yields a polymer.

The IR spectrum of compound VI has two very strong bands at 2203 and 2180 cm^{-1}. The ν(NC) stretching frequencies are shifted to relatively high wavenumbers (see Experimental) compared with those of $[Pt_3(CNC_6H_3\text{-}2,6\text{-}Me_2)_6]$. Since the ν(NC) stretching frequencies in the IR spectrum of the cationic platinum(II) complexes $[PtR(PPh_3)_2(CNBu^t)_2]^+X^-$ ($RX = I_2$, CH_3F, CF_3I) fall in the range of 2225–2190 cm^{-1}, the oxidation state of platinum in compound VI appears to be close to two [21,22].

Reactions of II with either chloro- or bromo-trifluoroethylene in diethyl ether at room temperature gave the vinyl palladium products VII and VIII, respectively, as expected [13]. Compounds VII and VIII were characterised by a elemental analysis and by IR and ^1H and ^{19}F NMR spectroscopy. These new complexes all showed IR and ^{19}F NMR spectra [16,23,24,25] characteristic of the presence of a $PdCF:CF_2$ group. The IR spectra of VII and VIII had, in addition to a band at ca. 1710 cm^{-1} characteristic of $CF:CF_2$, a single sharp ν(NC) stretching frequency, thus confirming a *trans*-configuration for the isocyanide ligands [7]. We found no evidence for initial formation of the three-membered ring (η^2) compounds in these reactions.

The olefins dimethyl fumarate (dmf) and maleic anhydride (ma) react with $[Pt_3(C_6H_3\text{-}2,6\text{-}Me_2)_6]$ and with II in diethyl ether at room temperature to affort the air stable complexes IX, X, XI and XII, respectively. These compounds were characterised by elemental analysis and by their ^1H and ^{13}C NMR spectra. The appearance of two ν(NC) bands in the IR spectrum of each complex supports the presence of two *cis* isocyanide ligands. The ^1H NMR spectrum of each of the four compounds shows a singlet between τ 7.54 and 7.58 ppm, which is evidence for two equivalent isocyanides with free rotation of the xylyl group. An interesting feature of

TABLE 1

ANALYTICAL DATA OF THE COMPLEXES I-XIV

Complex	M.p. [a] (°C)	Colour	Yield (%)	Analyses (Found (calcd.) (%))		
				C	H	N
I	144	red	90	29.1 (28.8)	4.4 (4.2)	8.6 (8.4)
II	152	red	75-91	58.6 (58.7)	4.9 (4.8)	7.6 (7.5)
III	120	white	67	41.8 (41.9)	3.3 (3.2)	4.8 (4.9)
IV	247	yellow	79	43.5 (42.9)	2.9 (2.7)	8.5 (8.3)
V	220	grey	93	48.6 (49.5)	3.1 (3.1)	9.2 (9.6)
VI	198-200	light-brown	69	48.8 (49.2)	3.2 (3.1)	13.9 (14.4)
VII	112	off-white	68	49.5 (49.5)	4.0 (3.7)	5.5 (5.7)
VIII	160-162	pale-yellow	68	45.2 (45.4)	3.6 (3.4)	5.2 (5.3)
IX	179	off-yellow	55	46.5 (47.9)	4.01 (4.4)	4.2 (4.7)
X	177-179	grey	86	55.6 (56.2)	5.2 (5.1)	5.3 (5.5)
XI	188	off-white	57	47.8 (47.6)	3.8 (3.6)	4.9 (5.0)
XII	203	grey	71	56.3 (56.6)	4.4 (4.3)	5.8 (6.0)
XIII	155	white	63	55.3 (56.7)	5.5 (4.9)	3.9 (4.3)
XIV	263	yellow	83	55.4 (54.6)	4.4 (4.1)	4.8 (5.0)

[a] With decomposition in vacuo, except for complexes III, VIII and X.

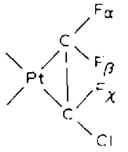
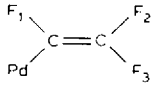
the ^{1}H NMR spectrum of X at room temperature, is a broad olefinic CH resonance for the dmf ligand. Moreover, on cooling (-60°C) a sharp single resonance was observed in the ^{13}C NMR spectrum at 50.8 ppm, assignable to the olefinic carbons of dmf.

In its ^{1}H NMR spectrum the platinum complex IX shows a sharp peak at τ 6.22 ppm assignable to olefinic hydrogens with ^{195}Pt–^{1}H coupling 62 Hz. Due to the low solubility, no ^{13}C NMR data are available for this species. On the other hand, the complexes XI and XII of maleic anhydride do not show broad olefinic resonances in their ^{1}H NMR spectra. In particular, the spectrum of the complex XI shows ^{195}Pt–^{1}H and ^{195}Pt–^{13}C coupling at room temperature of 61 and 254 Hz, respectively, as expected for such complexes [14]. The olefinic protons are less shielded in the palladium complexes (Table 3). In the IR spectrum the ν(NC) stretching frequencies are higher in the platinum complexes than in the palladium analogues (see Experimental).

It seemed likely that the reaction between $[Pt_3(CNC_6H_3\text{-}2,6\text{-}Me_2)_6]$ and the compound $HSiMePh_2$ in diethyl ether at room temperature might follow a different path from that between $[Pt_3(CNBu^t)_6]$ and $HSiMePh_2$ [15]. However, the white air

TABLE 2

^{19}F NMR CHEMICAL SHIFTS (ppm)[a] AND COUPLING CONSTANTS (Hz)

Complex						
	δ_α	δ_β	δ_χ	$J_{\alpha\beta}$	$J_{\alpha\chi}$	$J_{\beta\chi}$
III[c,d]	115.5 (293)	116.7 (250)	139.4 (212)	187	1	55
	δ					
IV[b,d]	55.5 (86)					
V[c]	55.2					
Complex						
	$\delta(1)$	$\delta(2)$	$\delta(3)$	$J_{1,2}$	$J_{1,3}$	$J_{2,3}$
VII[b]	147.8	95.8	125.4	52	116	100
VIII[b]	147.4	95.5	124.7	54	115	100

[a] Relative to CCl_3F (δ 0.0 ppm). [b] Measured in $CHCl_3$. [c] Measured in thf. [d] J(PtF) in ( ) in Hz.

stable product XIII is formulated as completely analogous to that obtained from the above reaction on the basis of the spectroscopic evidence. In particular, the IR spectrum shows only one very strong band at 2159 cm^{-1} attributable to terminal isocyanides. It is known that the absence of two such absorptions indicates that *cis*-[$Pt(CNC_6H_3$-2,6-$Me_2)_2$] groups are not present. A band of medium intensity at 1522 cm^{-1} indicates the presence of a C:N group.

The ^{1}H NMR spectrum of complex XIII shows a single resonance at τ -0.22 ppm suggesting the existence of an imidoyl ligand (Pt · *CH*:NR), and two sets of ^{1}H–^{195}Pt couplings (179 and 73 Hz), showing that compound XIII is a diplatinum species. Unfortunately, we were unable to see any satellites due to molecules with two ^{195}Pt nuclei. The ^{13}C NMR spectrum shows a resonance at 212.1 ppm which is tentatively attributed to the carbon σ-bonded to platinum, since it has J(PtC) 1036 Hz [22], but the assignment is uncertain because the peaks are very weak.

The same reasoning as applied to the previous reaction, prompted a study of the interaction between [$Pt_3(CNC_6H_3$-2,6-$Me_2)_6$] and cyclopropenone in toluene at room temperature. This reaction gave a yellow solid XIV. Elemental analysis and the ^{1}H NMR spectrum shows XIV to be completely analogous to the product of the reaction of [$Pt_3(CNBu^t)_6$] with cyclopropenone [11]. (Due to low solubility, no ^{13}C NMR data are available for compound XIV.) In particular, the IR spectrum had two very strong bands at 2150 and 2120 cm^{-1} assignable to two terminal *cis*-isocyanides, and there is also an absorption at 1570 cm^{-1} attributable to a bridging carbonyl group. In the aromatic region of the ^{1}H NMR spectrum of the complex XIV, there are two multiplets, at τ 1.74 and 2.96 ppm, assignable to the hydrogens of the phenyls and to the aromatic protons of the isocyanide ligands, respectively. A single resonance at τ 7.90 ppm indicates the equivalence of the four isocyanide ligands.

Experimental

General

NMR spectra [^1H, ^{19}F, and ^{13}C-{^1H}] were recorded on JEOL PFT and PS 100 spectrometers with ^{13}C shifts relative to $SiMe_4$(0.0 ppm) and ^{19}F shifts relative to CCl_3F (0.0 ppm). Infrared spectra were recorded with Nujol mulls on a Perkin–Elmer 457 spectrophotometer. Reactions were carried out using Schlenk-tube techniques under dry oxygen-free nitrogen, with solvents dried and distilled under nitrogen before use. The complexes [$Pt_3(CNBu^t)_6$], [$Pd(dba)_2$] [26], and [$Pd_2(dba)_3CHCl_3$] [27] were prepared by literature methods. Analytical and other data for the new compounds are given in Table 1. ^{19}F, ^1H and ^{13}C {^1H}-decoupled NMR data are given in Tables 2 and 3.

Synthesis of the complex I

The compound Pr^iNC (0.08 g, 1.2 mmol) in light petroleum (5 cm^3) was treated with [$Pt(cod)_2$] (0.21 g, 0.5 mmol), which was added as finely powdered solid in portions (ca. 0.1 g) with stirring. After a rapid reaction the orange precipitate was allowed to settle, and then washed with light petroleum to give red crystals of [$Pt_3(CNPr^i)_6$] (I) (0.45 g), dried in vacuo (ν_{max}(NC) 2130vs and 2033m cm^{-1}).

Synthesis of the complex II

The isocyanide CNC_6H_3-2,6-Me_2 (0.66 g, 5.0 mmol) in hexane (20 cm^3) was treated with [$Pd(dba)_2$] (1.15 g, mmol), which was added in portions. The mixture was stirred (0.25 h) at room temperature forming a yellow precipitate. The volatile material was removed in vacuo and after the addition of diethyl ether (180 cm^3) and further stirring (0.5 h), the mixture gave a red precipitate which was allowed to settle. The supernatant liquid was decanted and the solid washed with diethyl ether (1 × 20 cm^3) to give red microcrystals of [$Pd(CNC_6H_3$-2,6-$Me_2)_6$] (II) (1.50–1.82 g), which were dried in vacuo. (ν_{max}(NC) 2093vs and 1911br). Compound II was similarly prepared from CNC_6H_3-2,6-Me_2 (0.17 g, 1.22 mmol) and [$Pd_2(dba)_3CHCl_3$] (0.26 g, 0.25 mmol).

Synthesis of complex III

Complex [$Pt_3(CNC_6H_3$-2,6-$Me_2)_6$] (0.34 g, 0.25 mmol) in toluene (50 cm^3) was treated with chlorotrifluoroethylene (2.0 mmol) in a tube fitted with a Westef stopcock. The mixture was stirred overnight to give a clear solution, which was concentrated in vacuo to (ca. 5 cm^3) giving white crystals of [$Pt(C_2F_3Cl)(CNC_6H_3$-2,6-$Me_2)_2$] (III) (0.23 g), which were dried in vacuo.

Samples of III undergo vinyl rearrangement when dissolved in acetone or chloroform. The ^{19}F NMR spectrum of III (chloroform-h_2) after 4 h at room temperature gave data (see Discussion and Table 2) in accord with the structure proposed, together with signals corresponding to a vinyl product.

Synthesis of complex IV

Compound [$Pt_3(CNC_6H_3$-2,6-$Me_2)_6$] (0.17 g, 0.13 mmol) was suspended in

TABLE 3

^{1}H AND ^{13}C NMR DATA [a]

Complex	^{1}H [b]	^{13}C [c]
I	5.88–6.16 (m, 6H, HCMe_2), 8.48 (d, 18H, Me_2CH), 8.68 (d, 18H, Me_2CH)	22.9 [s(br), CH(Pr^i)], 21.3 [s(br), Me]
II	3.06[s(br), 18H], 7.82[s(br), 36H, Me]	
III	2.68–2.92 (m, 6H, C_6H_3), 7.54 (d, 12H, Me)	
IV	2.62–2.85 (m, 6H, C_6H_3), 7.50 (d, 12H, Me)	
V	2.59–2.88 (m, 6H, C_6H_3), 7.52 (d, 12H, Me)	
VI	2.57–2.87 (m, 6H, C_6H_3), 7.49 (s, 12H, Me)	136.4, 131.3, 130.7, 130.1, 129.5, 128.8 (Ph) 113.3 [NCC, *J*(PtC) 49], 18.9 (Me)
VII	2.58–2.85 (m, 6H, C_6H_3), 7.50 (s, 12H, Me)	
VIII	2.58–2.88 (m, 6H, C_6H_3), 7.49 (s, 12H, Me)	156.7 (CN), 136.5, 130.7, 129.9, 128.2 (Ph) 18.6 (Me)
IX	2.70–2.96 (m, 6H, C_6H_3), 6.22[s, 2H, HC, *J*(PtH) 62], 6.34 (s, 6H, OMe), 7.58 (s, 12H, Me)	
X	2.72–2.98 (m, 6H, C_6H_3), 5.71 (s(br), 2H, CH), 6.38 (s, 6H, OMe), 7.56 (s, 12H, Me)	172.8 (C=O), 157.9 (CN), 135.1, 128.9, 127.9 (Ph, 51.1 (OMe)
XI	2.68–2.95 (m, 6H, C_6H_3), 6.14[s, 2H, HC, *J*(PtH) 61], 7.57 (s, 12H, Me)	172.8[C=O, *J*(PtC) 43], 135.3, 129.5, 128.2 (Ph), 37.7[CH, *J*(PtC) 254], 18.8 (Me)
XII	2.68–2.96 (m, 6H, C_6H_3), 5.66 (s, 2H, HC), 7.54 (s, 12H, Me)	171.2 (C=O), 155.3 (CN), 135.5, 129.7, 128.2 (Ph), 49.7 (CH), 18.9 (Me)
XIII	-0.22[s, 2H, HC, *J*(PtH) 179.73], 2.24–2.32 (m, Ph), 8.07 (s, 12H, Me), 8.34 (s, 12H, Me), 9.23 [s, 6H, *J*(PtH) 32, SiMe]	212.1 [PtCH, *J*(PtC) 1036.55], 145.6 (Ph(C^1)Si), 144.5[Ph(C^1)Si, *J*(PtC) 28], 135.6 (Ph or C_6H_3), 135.2 [Ph(C^2)Si, J(PtC) 24], 134.4, 129.5, 127.8, 126.9 (Ph or C_6H_3), 18.8, 18.0 (Me), 0.61 (MeSi)
XIV	1.68–1.76 (m, 4H, *O*-$H_2C_6H_3$), 2.76–3.18 (m, 2H, P-HC_6H_4, 4H, m-$H_2C_6H_3$, 12H, C_6H_3), 7.90 (s, 24H, Me)	

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[a] Measured in $CDCl_3$ at room temperature, unless otherwise stated. Coupling constants in Hz. [b] Chemical shifts (τ) in ppm. [c] ^{1}H decoupled, chemical shifts in ppm to high frequency of $SiMe_4$. [d] The ^{13}C NMR spectra of the complexes VI and XIII were measured in CH_2Cl_2 and in C_6H_6, respectively.

diethyl ether (5 cm^3) and 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene (0.24 g, 1.14 mmol) was added slowly. The mixture was stirred (1 h) at room temperature, and then filtered. The residue was washed with diethyl ether (2 × 3 cm^3) to give yellow microcrystals of $[Pt\{(CN)_2C{:}C(CF_3)_2\}(CNC_6H_3\text{-}2,6\text{-}Me_2)_2]$ (IV) (0.13 g), which were dried in vacuo (ν_{max}(CN) 2267s and ν(NC) 2230vs, 2218vs).

Synthesis of complex V

A suspension of complex II (0.22 g, 0.2 mmol) in diethyl ether (10 cm^3) was treated with 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene (0.13 g, 0.6 mmol) which was added slowly at room temperature with stirring. After a rapid change in colour and further stirring (0.5 h), the mixture gave a grey residue which was allowed to settle. The supernatant solution was removed and the solid washed with hexane (2 × 3 cm^3) to give grey microcrystals of $[Pd\{(CN)_2C{:}C(CF_3)_2\}(CNC_6H_3\text{-}2,6\text{-}Me_2)_2]$ (V) (0.20 g), which were dried in vacuo. (ν_{max}(CN) 2203s and ν(NC) 2185sh, 2175vs).

Synthesis of complex VI

The compound $(CN)_3C{:}C(CN)_2$ (0.01 g, 0.75 mmol) was added portion wise to a vigorously stirred suspension of $[Pt_3(CNC_6H_3\text{-}2,6\text{-}Me_2)_6]$ (0.34 g, 0.25 mmol) in diethyl ether (10 cm^3), and the mixture was stirred for 1 h. The heavy brown precipitate produced was filtered off and washed with diethyl ether (2 × 3 cm^3) to give light brown microcrystals of $[Pt\{C_2(CN)_4\}(CNC_6H_3\text{-}2,6\text{-}Me_2)_2]$ (VI) (0.23 g), which was dried in vacuo (ν_{max}(CN) 2232s and ν(NC) 2203vs, 2180vs).

Synthesis of complexes VII and VIII

Complex II (0.15 g, 0.14 mmol) in diethyl ether (40 cm^3) was treated with chlorotrifluoroethylene (2.5 mmol) in a tube fitted with a Westef stopcock. The mixture was stirred for 0.5 h to give a clear solution, which was filtered. The filtrate was concentrated to a small volume (ca. 4 cm^3) to give off-white crystals of $[Pd(Cl)(C_2F_3)(CNC_6H_3\text{-}2,6\text{-}Me_2)_2]$ (VII) (0.10 g), which were dried in vacuo. (ν_{max}(NC) 2210vs and ν(C=C) 1710s). The compound $[Pd(Br)(C_2F_3)(CNC_6H_3\text{-}2,6\text{-}Me_2)_2]$ (VIII) was prepared from II (0.28 g, 0.25 mmol) and bromotrifluoroethylene (2.5 mmol). (ν_{max}(NC) 2202vs and ν(C=C) 1718s).

Synthesis of complexes IX–XII

All these were prepared in a similar way, and the following example is representative.

Addition of compound II (0.28 g, 0.25 mmol) at room temperature to a solution of dimethyl fumarate (0.108 g, 0.75 mmol) in diethyl ether (10 cm^3) led to an immediate change in colour from red to grey. After stirring (0.5 h) the mixture gave a residue, which was washed with diethyl ether (3 × 3 cm^3) to give grey microcrystals of $[Pd(dmf)(CNC_6H_3\text{-}2,6\text{-}Me_2)_2]$ (X) (0.24 g), which was dried in vacuo. (ν_{max}(NC) 2126 vs, 2151vs and ν(C=C) 1682vs).

The reaction between II (0.28 g, 0.25 mmol) and maleic anhydride (ma) (0.15 g, 2.5 mmol) gave $[Pd(ma)(CNC_6H_3\text{-}2,6\text{-}Me_2)_2]$ (XII). (ν_{max}(NC) 2165vs, 2140vs, and ν(C=O) 1798vs).

Complexes $[Pt(dmf)(CNC_6H_3\text{-}2,6\text{-}Me_2)_2]$ (IX) (ν_{max}(NC) 2167vs, 2132vs and ν(C=O) 1701vs] and $[Pt(ma)(CNC_6H_3\text{-}2,6\text{-}Me_2)_2]$ (XI) (ν_{max}(NC) 2183vs, 2152vs and ν(C=O) 1807vs) were prepared in the same manner. For complex XII the order of mixing of the starting materials was reversed, and the stirring time for complexes IX and XI was 48 and 16 h, respectively.

Synthesis of complex XIII

The complex $[Pt_3(CNC_6H_3\text{-}2,6\text{-}Me_2)_6]$ (0.34 g, 0.25 mmol) was suspended in diethyl ether (10 cm^3) in a Schlenk tube and diphenylmethylsilane (0.15 g, 0.75 mmol) was added from a syringe. After two days stirring at room temperature the white solid formed was washed with hexane (2×3 cm^3) and crystallised from thf/diethyl ether to give white crystals of $[\{Pt(CH{:}NC_6H_3\text{-}2,6\text{-}Me_2)\cdot(SiMePh_2)(CNC_6H_3\text{-}2,6\text{-}Me_2\}_2]$ (XIII) (0.21 g), which were dried in vacuo. (ν_{max}(NC) 2169sh, 2159vs and ν(C=N) 1522m).

Synthesis of complex XIV

A solution of $[Pt_3(CNC_6H_3\text{-}2,6\text{-}Me_2)_6]$ (0.34 g, 0.25 mmol) in toluene (15 cm^3) was treated dropwise with a toluene solution of diphenylcyclopropenone (0.08 g, 0.38 mmol). The mixture was stirred overnight at room temperature to give the yellow solid $[Pt_2\{\mu\text{-}(PhC)_2CO\}(CNC_6H_3\text{-}2,6\text{-}Me_2)_4]$ (XIV) (0.28 g), which was dried in vacuo. (ν_{max}(NC) 2150vs, 2120vs and ν(C=O) 1586s, 1570vs).

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