

Isocyanide and Diisocyanide Complexes of a Tripalladium Cluster

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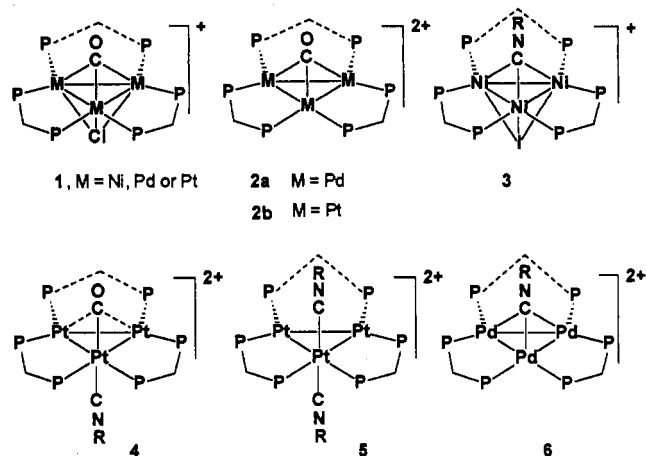
Received September 16, 1993*

New cluster complexes derived from the reactions of $[\text{Pd}_3(\mu_3\text{-CO})(\mu\text{-dppm})_3]^{2+}$, **2a**, with $\text{XyN}\equiv\text{C}$ ($\text{Xy} = 2,6\text{-C}_6\text{H}_3\text{Me}_2$) and $1,4\text{-C}\equiv\text{NCMe}_4\text{N}\equiv\text{C}$ are reported. Reaction of XyNC with **2a** gives $[\text{Pd}_3(\mu_3\text{-}\eta^1\text{-CNXy})(\mu\text{-dppm})_3]^{2+}$, **6**, which contains the very unusual $\mu_3\text{-}\eta^1$ -bonding mode of the isocyanide and which has been characterized crystallographically [monoclinic, $P2_1/n$, $a = 13.624(1)$ Å, $b = 42.373(3)$ Å, $c = 14.025(1)$ Å, $\beta = 98.78(5)^\circ$, $Z = 4$, $R = 0.0597$, $R_w = 0.0641$]. This 42-electron cluster reversibly adds XyNC to form the 44-electron cluster $[\text{Pd}_3(\mu_3\text{-}\eta^1\text{-CNXy})_2(\mu\text{-dppm})_3]^{2+}$. Reaction of **2a** or **6** with $1/2$ equiv of the diisocyanide ligand $1,4\text{-C}_6\text{Me}_4(\text{NC})_2$ gave the complex cation $\{[\text{Pd}_3(\mu\text{-dppm})_3]_2(\text{CNC}_6\text{Me}_4\text{NC})\}[\text{PF}_6]_4$, **8**, with displacement of CO or XyNC respectively. Reaction of **2a**, as either the $[\text{PF}_6]^-$ or CF_3CO_2^- salt, with 1 equiv of $1,4\text{-C}_6\text{Me}_5(\text{NC})_2$ gave the corresponding complex $\{[\text{Pd}_3(\text{CNC}_6\text{Me}_4\text{NC})(\mu\text{-dppm})_3]_2\text{X}_2\}_n$, **9**. In **8**, the diisocyanide bridges between Pd_3 cluster units, using the same $\mu_3\text{-}\eta^1$ -bonding mode as in **6**, but in **9** partial dissociation leads to some monodentate diisocyanide units. The palladium clusters with isocyanides tend to adopt the 42-electron configuration with triply bridging isocyanides and are different from the platinum analogs, for which the 44-electron configuration with terminal isocyanides is strongly preferred, and the nickel complexes, for which a 48-electron configuration with triply bridging isocyanide is preferred.

Introduction

The trinuclear clusters of nickel, palladium, and platinum display many differences in structure and reactivity.¹⁻³ For example, Ni_3 clusters are usually coordinatively saturated while Pd_3 and Pt_3 clusters are not. Most often, Pd_3 and Pt_3 clusters have a 42-electron configuration with the valence p_z orbital on each metal vacant.^{2b} The only complete triad of isostructural clusters is the series $[\text{M}_3\text{Cl}(\mu_3\text{-CO})(\mu\text{-dppm})_3]^+$, **1**, with $\text{M} = \text{Ni}$, Pd , and Pt and $\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$, which is based on the $[\text{M}_3(\mu\text{-dppm})_3]^{2+}$ triangle capped on either side by μ_3 -carbonyl and halide ligands.⁴ Formally these are 48-electron, coordinatively saturated clusters although coordinative unsaturation is easily achieved when $\text{M} = \text{Pd}$ or Pt by partial or complete dissociation of the halide ligand.^{5,6} Even with clusters based on the $[\text{M}_3(\mu\text{-dppm})_3]^{2+}$ core, there are differences in properties, with nickel often the exception. For example, the monocapped, 42-electron clusters $[\text{M}_3(\mu_3\text{-CO})(\mu\text{-dppm})_3]^{2+}$, **2**, are easily prepared when $\text{M} = \text{Pd}$ or Pt but not when $\text{M} = \text{Ni}$.⁴⁻⁶ A particularly interesting difference between nickel and platinum is observed with isocyanide ligands. Nickel forms the 48-electron cluster $[\text{Ni}_3(\mu_3\text{-I})(\mu_3\text{-}\eta^1\text{-CNR})(\mu\text{-dppm})_3]^+$, **3**, $\text{R} = \text{Me}$,⁷ while platinum forms the 44-electron clusters $[\text{Pt}_3(\mu_3\text{-CO})(\text{CNR})(\mu\text{-dppm})_3]^{2+}$, **4**, and $[\text{Pt}_3\text{-}$

$(\text{CNR})_2(\mu\text{-dppm})_3]^{2+}$, **5**, $\text{R} = \text{Me}$ or Xy and $\text{Xy} = 2,6\text{-dimethylphenyl}$.⁸ With nickel the isocyanide adopts the very unusual $\mu_3\text{-}\eta^1$ -bonding mode⁷ while with platinum only terminal isocyanides are formed.⁸ It was of interest to determine how the corresponding palladium clusters behave with isocyanide ligands. This article reports that palladium is different from both nickel and platinum in forming the 42-electron cluster $[\text{Pd}_3(\mu_3\text{-}\eta^1\text{-CNR})(\mu\text{-dppm})_3]^{2+}$, **6**, $\text{R} = \text{Xy}$, and also reports the first derivatives with diisocyanide ligands acting as bis(triply bridging) ligands. These too are different from the analogous platinum complexes.⁹



Results

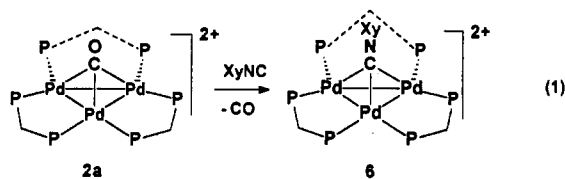
Formation and Characterization of the Cluster Cation $[\text{Pd}_3(\mu_3\text{-}\eta^1\text{-CNXy})(\mu\text{-dppm})_3]^{2+}$. The reaction of XyNC with $[\text{Pd}_3(\mu_3\text{-CO})(\mu\text{-dppm})_3]^{2+}$, **2a**, occurred according to eq 1. In this reaction, addition of XyNC occurs with displacement of CO and formation of the 42-electron cluster cation **6**, in contrast to the corresponding reaction with the platinum complex **2b** in which the CO remains in the 44-electron cluster cation **4**.^{8,9} No

* Abstract published in *Advance ACS Abstracts*, March 1, 1994.

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intermediate could be detected in the palladium reaction, again in contrast to the analogous platinum reaction,⁸ and **6** failed to form a CO adduct analogous to **4** even in the presence of excess CO. The structure of cation **6**, as the $[\text{PF}_6]^-$ salt, was determined crystallographically and is shown in Figure 1. Selected bond distances and angles are given in Table 1.

The structure of the cation contains a triangle of palladium atoms, in which the Pd–Pd distances range from 2.593(1) to 2.651(1) Å, with the isocyanide as a $\mu_3\text{-}\eta^1$ -bridging ligand. The Pd–C distances [2.15(1)–2.18(1) Å] and Pd–C–Pd angles [73.8(5)–75.6(5) $^\circ$] are almost equal, as expected for a symmetrical triply bridging ligand. The isocyanide is distorted from linearity with angle $\text{C}\equiv\text{N}-\text{C} = 167(1)^\circ$, very similar to that of 164.6(9) $^\circ$ in the nickel cluster **3**.⁷ Nevertheless, it is clearly closer to the geometry expected for “sp” linear than for the alternative “sp²” bend structure. The $\text{N}\equiv\text{C}$ distances are identical in **3** and **6** at 1.17(1) and 1.17(2) Å, respectively.⁷

Two of the μ -dppm ligands adopt envelope conformations with the CH_2 flaps toward the XyNC ligand, and only one has the CH_2 flap away. Hence only the phenyl groups defined by *ipso* carbon atoms C(111) and C(211) are axial on the XyNC side of the $\text{Pd}_3(\text{dppm})_3$ unit, and steric hindrance is reduced compared to the other side.³ Steric hindrance is further relieved by distortion of the phosphorus donors below the Pd_3 plane. There is a propellerlike arrangement in which alternate phosphorus donors P(2), P(4), and P(6) are furthest below the Pd_3 plane. As a result, there is a wide range of angles $\text{C}(1)\text{PdP}$ from 113.0(4) $^\circ$ for P(5) to 130.0(4) $^\circ$ for P(4). We note that this is the first structure determination for a 42e cluster based on the $\text{Pd}_3(\mu\text{-dppm})_3$ unit. The analogous carbonyl cluster $[\text{Pd}_3(\mu_3\text{-CO})(\mu\text{-dppm})_3]^{2+}$ tends to add an anionic ligand below the Pd_3 unit, and structures of the adducts with CF_3CO_2^- , Cl^- , and I^- have been reported.⁵ In addition, $[\text{Pd}_3(\mu_3\text{-PF}_3)(\mu\text{-dppm})_3]^{2+}$ also exists as the adduct with Cl^- .^{7c} It is not clear why the combination of isocyanide ligand and Pd_3 cluster leads to this preference for a 42-electron count, when the isocyanide with Ni_3 or Pt_3 clusters or the Pd_3 cluster with CO or PF_3 all give higher electron counts.^{5–10} Nevertheless, this is the case and further confirmation will be found in reactions described below.

In the IR spectrum, complex **6** as a Nujol mull gives $\nu(\text{N}\equiv\text{C}) = 1968$ (s), 1989 (m) cm^{-1} . The two peaks appear to be due to solid state splitting or to the presence of different crystalline forms since only one band at 1972 cm^{-1} is observed in CH_2Cl_2 solution. The nickel complex **3** has $\nu(\text{N}\equiv\text{C}) = 1922$ cm^{-1} and, even though the isocyanides are different, the difference in $\nu(\text{N}\equiv\text{C})$ stretching frequencies of 50 cm^{-1} shows clearly that back-bonding from the metal to π^* -orbitals of the isocyanide is weaker for palladium than for nickel.⁷ For the isostructural carbonyl clusters **1** there is an even bigger difference with $\nu(\text{CO}) = 1717$ and 1820 cm^{-1} for $\text{M} = \text{Ni}$ and Pd respectively.^{4,5} Back-bonding appears to be much weaker to the $\mu_3\text{-}\eta^1\text{-CNR}$ ligand in **3** or **6** compared to the CO ligand in the analogous carbonyl clusters **1**. Note that $\nu(\text{N}\equiv\text{C})$ for free XyNC occurs at 2121 cm^{-1} , and $\nu(\text{N}\equiv\text{C})$ for the terminal isocyanides in **4** and **5** are 2131 and 2122 cm^{-1} , respectively, similar or slightly shifted to higher energy compared to the free ligand.⁸ Since a much greater shift to lower energy (300–600 cm^{-1}) is observed for $\nu(\text{N}\equiv\text{C})$ in bent $\mu\text{-CNR}$ ligands,^{1,10} the $\nu(\text{NC})$ frequency appears to be useful, at least as

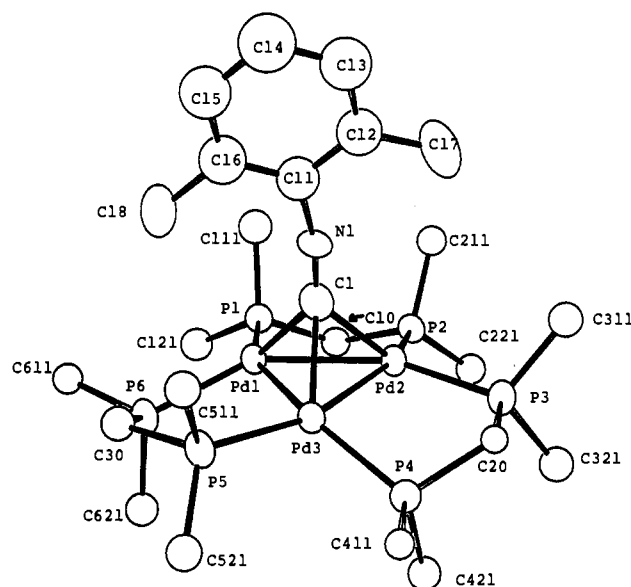


Figure 1. View of the structure of the cluster cation **6**, with the atomic labeling scheme. Only the *ipso* carbon atoms of the dppm phenyl groups are shown, for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) for $6[\text{PF}_6]_2$

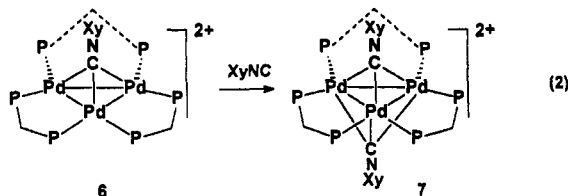
Pd(1)–Pd(2)	2.651(1)	Pd(1)–Pd(3)	2.593(1)
Pd(2)–Pd(3)	2.617(1)		
Pd(1)–P(1)	2.306(4)	Pd(2)–P(2)	2.364(4)
Pd(2)–P(3)	2.330(4)	Pd(3)–P(4)	2.300(4)
Pd(3)–P(5)	2.291(3)	Pd(1)–P(6)	2.331(3)
Pd(1)–C(1)	2.15(1)	Pd(2)–C(1)	2.18(1)
Pd(3)–C(1)	2.17(1)	C(1)–N(1)	1.17(2)
N(1)–C(11)	1.40(1)	C(12)–C(17)	1.50(2)
C(16)–C(18)	1.53(2)	P(1)–C(111)	1.83(1)
P(1)–C(121)	1.82(1)	P(2)–C(211)	1.80(1)
P(2)–C(221)	1.82(1)	P(3)–C(311)	1.82(1)
P(3)–C(321)	1.82(1)	P(4)–C(411)	1.81(1)
P(4)–C(421)	1.81(1)	P(5)–C(511)	1.81(1)
P(5)–C(521)	1.82(1)	P(6)–C(611)	1.82(1)
P(6)–C(621)	1.82(1)	P(1)–C(10)	1.85(1)
P(2)–C(10)	1.86(1)	P(3)–C(20)	1.85(1)
P(4)–C(20)	1.84(1)	P(5)–C(30)	1.84(1)
P(6)–C(30)	1.84(1)		
Pd(3)–Pd(1)–Pd(2)	59.85(4)	Pd(3)–Pd(2)–Pd(1)	58.99(4)
Pd(2)–Pd(3)–Pd(1)	61.16(4)	P(1)–Pd(1)–Pd(2)	94.2(1)
P(1)–Pd(1)–Pd(3)	153.4(1)	P(6)–Pd(1)–Pd(2)	147.3(1)
P(6)–Pd(1)–Pd(3)	91.5(1)	P(2)–Pd(2)–Pd(1)	95.6(1)
P(2)–Pd(2)–Pd(3)	152.5(1)	P(3)–Pd(2)–Pd(1)	151.4(1)
P(3)–Pd(2)–Pd(3)	92.6(1)	P(4)–Pd(3)–Pd(1)	148.4(1)
P(4)–Pd(3)–Pd(2)	94.5(1)	P(5)–Pd(3)–Pd(1)	97.3(1)
P(5)–Pd(3)–Pd(2)	158.3(1)	C(1)–Pd(1)–Pd(2)	52.7(4)
C(1)–Pd(1)–Pd(3)	53.5(4)	C(1)–Pd(2)–Pd(1)	51.7(4)
C(1)–Pd(2)–Pd(3)	52.9(4)	C(1)–Pd(3)–Pd(1)	52.6(4)
C(1)–Pd(3)–Pd(2)	53.1(4)	P(6)–Pd(1)–P(1)	111.1(1)
P(3)–Pd(2)–P(2)	111.4(1)	P(5)–Pd(3)–P(4)	106.5(1)
C(1)–Pd(1)–P(1)	117.1(4)	C(1)–Pd(1)–P(6)	124.4(4)
C(1)–Pd(2)–P(2)	121.4(4)	C(1)–Pd(2)–P(3)	115.9(4)
C(1)–Pd(3)–P(4)	130.0(4)	C(1)–Pd(3)–P(5)	113.0(4)
C(10)–P(1)–Pd(1)	112.3(5)	C(10)–P(2)–Pd(2)	110.8(4)
C(20)–P(3)–Pd(2)	113.9(4)	C(20)–P(4)–Pd(3)	107.4(4)
C(30)–P(5)–Pd(3)	113.1(4)	C(30)–P(6)–Pd(1)	111.4(4)
P(2)–C(10)–P(1)	111.0(7)	P(4)–C(20)–P(3)	108.1(6)
P(6)–C(30)–P(5)	111.9(7)	Pd(2)–C(1)–Pd(1)	75.6(5)
Pd(3)–C(1)–Pd(1)	73.8(5)	Pd(3)–C(1)–Pd(2)	74.0(5)
N(1)–C(1)–Pd(1)	137(1)	N(1)–C(1)–Pd(2)	136(1)
N(1)–C(1)–Pd(3)	133.2(12)	C(11)–N(1)–C(1)	167(1)
C(17)–C(12)–C(13)	117.7(8)	C(17)–C(12)–C(11)	122.3(8)
C(18)–C(16)–C(15)	120.3(7)	C(18)–C(16)–C(11)	119.7(7)
C(12)–C(11)–N(1)	118.3(6)	C(16)–C(11)–N(1)	121.6(6)

a preliminary indication of the binding mode of an isocyanide ligand. For the nickel group elements, a small shift to low energy (150–200 cm^{-1}) compared to $\nu(\text{NC})$ for the free isocyanide is indicative of the linear $\mu_3\text{-}\eta^1\text{-CNR}$ ligand.

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Complex **6** gave a single resonance in the ^{31}P NMR spectrum due to the dppm phosphorus atoms and a very broad unresolved resonance due to the CH_2 protons [two resonances are expected since there is no plane of symmetry containing the $\text{Pd}_3(\text{dppm})_3$ unit]. The methyl protons of the XyNC ligand gave a sharp singlet in the ^1H NMR. Thus, the molecule appears to have C_{3v} symmetry on the NMR time scale, as expected if the xylyl group can rotate easily.

Formation and Characterization of the Cluster Cation $[\text{Pd}_3(\mu_3\text{-}\eta^1\text{-CNXy})_2(\mu\text{-dppm})_3]^{2+}$, **7**. Reaction of **6** with a further equivalent of XyNC in dichloromethane solution gave a shift in the ^{31}P NMR resonance of the dppm ligands from -6.7 to -8.4 ppm and evaporation of the solution, followed by thorough washing with *n*-pentane, gave the bis(isocyanide) cluster cation $[\text{Pd}_3(\mu_3\text{-}\eta^1\text{-CNXy})_2(\mu\text{-dppm})_3]^{2+}$, **7** (eq 2). The same complex was formed



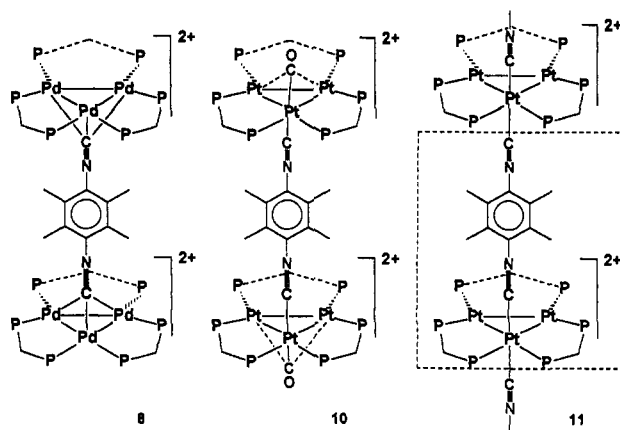
by reaction of **2a** with 2 equiv of XyNC . The cluster as the $[\text{PF}_6]^-$ salt gave a satisfactory elemental analysis and the presence of the $\mu_3\text{-}\eta^1\text{-CNXy}$ was indicated by IR bands at 1967 cm^{-1} and 2014 cm^{-1} . However, on attempted recrystallization of **7** under several sets of conditions, the extra XyNC ligand dissociated with formation of crystals of **6**. Hence crystallographic characterization of **7** was not possible.

The $\nu(\text{N}\equiv\text{C})$ stretching frequencies for **7** clearly indicate the bridging isocyanide ligand, and the structure is therefore different from that of the platinum analog **5**, which has terminal isocyanides.⁸ The XyNC ligands in **5** migrate rapidly around the Pt_3 triangle, and a structure completely analogous to **7** has been proposed as the transition state.⁸ Complex **5** is thermally very stable with no tendency to dissociation whereas the new complex **7** easily dissociates the second XyNC ligand. Compared to platinum therefore, the palladium cluster has a greater tendency to adopt the 42- rather than the 44-electron configuration and the $\mu_3\text{-CNR}$ ligand is stabilized with respect to terminal CNR.

Cluster Cations with Diisocyanide Ligands. There has been much interest in conjugated, "rigid-rod" polymers with bridging diisocyanide ligands, but very few of these contain metal-metal bonds.¹¹ The successful isolation of clusters **6** and **7** suggested that binuclear or polymeric clusters might be obtained in which a linear diisocyanide bridges between Pd_3 units.

Reaction of either **2a** or **6** $[\text{PF}_6]_2$ with $1/2$ equiv of the diisocyanide ligand $1,4\text{-C}_6\text{Me}_4(\text{NC})_2$ gave the complex cation $[\{\text{Pd}_3(\mu\text{-dppm})_3\}]_2(\text{CNC}_6\text{Me}_4\text{NC})[\text{PF}_6]_4$, **8**. The complex was moisture sensitive presumably due to enhanced reactivity due to polarization of the isocyanide ligand. The IR spectrum of **8** contains a band at 1958 cm^{-1} , in support of the proposed structure in which each isocyanide acts as a linear triply bridging ligand to a Pd_3 unit and the ligand therefore bridges between two Pd_3 cluster units. An unexpected feature of **8** is that the ^{31}P NMR spectrum contained three broad resonances due to the dppm phosphorus atoms whereas, by analogy to **6**, only one would be expected. To obtain apparent 3-fold symmetry, the aryl unit of the diisocyanide ligand must be able to spin rapidly about the $\text{CN}\cdots\text{CN}$ axis. Perhaps this rotation is restricted by interaction with dppm phenyl substituents in the sterically crowded **8** with the resulting nonequivalence of phosphorus atoms.

Reaction of **2a**, as either the $[\text{PF}_6]^-$ or CF_3CO_2^- salt, with 1 equiv of $1,4\text{-C}_6\text{Me}_4(\text{NC})_2$ gave the corresponding complex



$[\{\text{Pd}_3(\text{CNC}_6\text{Me}_4\text{NC})(\mu\text{-dppm})_3\}\text{X}_2]_n$, **9**. These complexes were also moisture sensitive. When $\text{X} = \text{PF}_6$, the IR spectrum contained strong bands at 1953 and 1988 cm^{-1} , which can be assigned to the linear $\mu_3\text{-}\eta^1\text{-CNR}$ linkage by comparison to **6** and **7**, and a weaker peak at 2161 cm^{-1} , which is close in energy to $\nu(\text{N}\equiv\text{C})$ in the free ligand (2121 cm^{-1}). When $\text{X} = \text{CF}_3\text{CO}_2$, the IR spectrum is similar, but the band at 2161 cm^{-1} is relatively stronger and there is an additional band at 1682 cm^{-1} due to trifluoroacetate. The ^{31}P NMR spectra of each salt contained two very broad resonances due to phosphorus atoms of dppm and the ^1H NMR spectra contained at least two broad resonances for the CH_2P_2 and ligand methyl resonances. These data suggest that the complexes occur as mixtures of oligomers and possibly monomer in solution and even in the solid state (Scheme 1, $n = \text{integer}$), with the better coordinating CF_3CO_2^- ligand giving a lower molecular weight species by competing with the second isocyanide donor. The coordination center (a Pd_3 triangle bridged by two $\mu_3\text{-}\eta^1\text{-CNR}$ donors) in the oligomeric form of **9** is analogous to that in **7**, and so it is not surprising that dissociation occurs easily. In support of this interpretation, recrystallization of **9** $[\text{PF}_6]_2$ led to loss of diisocyanide ligand and formation of $[\{\text{Pd}_3(\mu\text{-dppm})_3\}]_2(\text{CNC}_6\text{Me}_4\text{NC})[\text{PF}_6]_4$, **8**.

The palladium chemistry with diisocyanides is different from platinum which forms the complex **10** and the polymer **11**, each having terminal isocyanide links and a 44-electron configuration.⁹

Experimental Section

Complexes **2a** $[\text{PF}_6]_2$ and **2a** $[\text{CF}_3\text{CO}_2]_2$ and the diisocyanide $1,4\text{-C}_6\text{Me}_4(\text{NC})_2$ were prepared by the literature methods.^{5,12} The XyNC was a commercial sample. NMR spectra were obtained by using Varian XL200 or XL300 spectrometers and were referenced to TMS (^1H) or H_3PO_4 (^{31}P).

$[\text{Pd}_3(\mu_3\text{-C}\equiv\text{NXy})(\mu\text{-dppm})_3][\text{PF}_6]_2$. To a solution of $[\text{Pd}_3(\mu_3\text{-CO})(\mu\text{-dppm})_3][\text{PF}_6]_2$ (100 mg) in CH_2Cl_2 (10 mL) was added XyNC (7.3 mg). After 5 min, the solvent was evaporated, and the residue was washed with *n*-pentane (5 mL) and recrystallized from CH_2Cl_2 /ether as dark red crystals. Yield: 85%. Mp $198\text{--}202\text{ }^\circ\text{C}$. Anal. Calcd for $\text{C}_{84}\text{H}_{75}\text{F}_{12}\text{N}_9\text{Pd}_3$: C, 53.2; H, 4.0; N, 0.7. Found: C, 52.8; H, 3.5; N, 0.5. NMR in acetone- d_6 : $\delta(^1\text{H}) = 2.22$ (s, 6H, Me), 5.18 (br, 6H, CH_2P_2); $\delta(^{31}\text{P}) = -6.7$ (s, dppm). IR (Nujol): $\nu(\text{C}\equiv\text{N}) = 1968, 1989\text{ cm}^{-1}$.

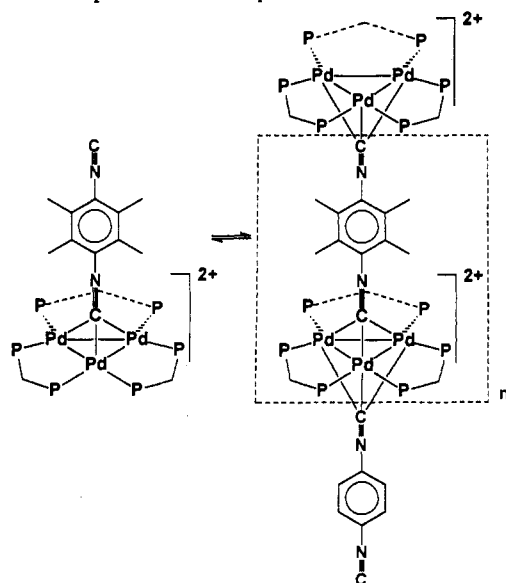
$[\text{Pd}_3(\mu_3\text{-C}\equiv\text{NXy})_2(\mu\text{-dppm})_3][\text{PF}_6]_2$. This was prepared similarly from $[\text{Pd}_3(\mu_3\text{-CO})(\mu\text{-dppm})_3][\text{PF}_6]_2$ (100 mg) in CH_2Cl_2 (15 mL) with XyNC (14.6 mg), except that it was not recrystallized. Yields: 98%. Mp: $153\text{--}156\text{ }^\circ\text{C}$. Anal. Calcd for $\text{C}_{93}\text{H}_{84}\text{F}_{12}\text{N}_{12}\text{Pd}_3$: C, 55.1; H, 4.1; N, 1.4. Found: C, 55.0; H, 3.6; N, 1.0. NMR in acetone- d_6 : $\delta(^1\text{H}) = 2.15$ (s, 12H, Me), 5.18 (br, 6H, CH_2P_2); $\delta(^{31}\text{P}) = -8.4$ (s, dppm). IR (Nujol): $\nu(\text{C}\equiv\text{N}) = 1967, 2014\text{ cm}^{-1}$. Attempted recrystallization gave **6** $[\text{PF}_6]_2$.

$[\{\text{Pd}_3(\mu\text{-dppm})_3\}]_2(\mu\text{-1,4-C}\equiv\text{NC}_6\text{Me}_4\text{N}\equiv\text{C})[\text{PF}_6]_4$. To a solution of $[\text{Pd}_3(\mu_3\text{-C}\equiv\text{NXy})(\mu\text{-dppm})_3][\text{PF}_6]_2$ (21 mg, 0.011 mmol) in CH_2Cl_2 (10 mL) was added $1,4\text{-C}_6\text{Me}_4(\text{NC})_2$ (1 mg, 0.055 mmol) in CH_2Cl_2 (2 mL). The solution was stirred for 10 min, the volume was reduced,

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Scheme 1. Equilibria in Complex 9



and *n*-pentane (10 mL) was added to precipitate a dark red solid. This was separated and recrystallized from acetone/pentane to give the product as dark red crystals. Yield: 55%. Mp: 183–185 °C. Anal. Calcd for $C_{162}H_{144}F_{24}N_2P_{16}Pd_6$: C, 52.4; H, 3.9; N, 0.8. Found: C, 51.3; H, 3.7; N, 0.7. NMR in acetone- d_6 : $\delta(^{31}P) = -6.6$ (br s), -6.7 (br s), -6.9 (br s), all dppm; $\delta(^1H) = 5.15$ (br s, 12H, CH_2P_2); 2.2 (br s, 12H, Me). IR (Nujol): $\nu(N\equiv C) = 1958$ cm^{-1} . The same product was obtained by similar reaction of **2a** with 1,4-CNC₆Me₄NC.

$\{[Pd_3(\mu-1,4-C\equiv NC_6Me_4N\equiv C)(\mu-dppm)_3][PF_6]_2\}_n$. To a stirred solution of $[Pd_3(\mu_3-CO)(\mu-dppm)_3][PF_6]_2$ (50 mg) in CH_2Cl_2 (2 mL) was added, 1,4-CNC₆Me₄NC (5.1 mg) in CH_2Cl_2 (1 mL). A dark red solid precipitated. The mixture was stirred for 1 h, and then allowed to stand overnight. Addition of *n*-pentane (10 mL) precipitated more red solid, which was separated by filtration, washed with *n*-pentane (3 mL), and dried under vacuum. Yield: 82%. Mp: 220–225 °C. Anal. Calcd for $C_{87}H_{78}F_{12}N_2P_8Pd_3$: C, 53.6; H, 4.0; N, 1.4. Found: C, 52.6; H, 3.6; N, 0.9. NMR in acetone- d_6 : $\delta(^{31}P) = -8.6$ (br s), -9.6 (br s, relative intensities 1:3, dppm); $\delta(^1H) = 1.6$ –2.6 (br s, 12H, Me), 5.05, 5.22 (br m, 6H, CH_2P_2). IR (Nujol): $\nu(N\equiv C) = 1953$, 1988 ($\mu_3-C\equiv NR$); 2161 (free $C\equiv NR$) cm^{-1} . Attempts to recrystallize this compound led to loss of diisocyanide and formation of $\{[Pd_3(\mu-dppm)_3]_2(\mu-1,4-C\equiv NC_6Me_4N\equiv C)-[PF_6]_4\}$.

Similarly, $\{[Pd_4(\mu-1,4-C\equiv NC_6Me_4N\equiv C)(\mu-dppm)_3][CF_3CO_2]_2\}_n$ was prepared from $[Pd_3(\mu_3-CO)(\mu-dppm)_3][CF_3]_2$ with 1,4-CNC₆Me₄NC in CH_2Cl_2 as a dark red solid. Yield: 75%. Mp: 192 °C. Anal. Calcd for $C_{91}H_{78}F_8N_2P_6O_4Pd_3 \cdot 3CH_2Cl_2$: C, 52.7; H, 3.9; N, 1.4. Found: C, 52.8; H, 4.0; N, 1.4. NMR in acetone- d_6 : $\delta(^{31}P) = -3.0$ [br s], -10.5 (br s, relative intensities 2:1, dppm), essentially unchanged at -80 °C; $\delta(^1H) = 1.6$ –2.3 (br s, 12H, Me), 4.0–5.1 (br m, 6H, CH_2P_2), 5.6 (s, 6H, CH_2Cl_2 of crystallization). IR (Nujol): $\nu(N\equiv C) = 1929$, 1958 ($\mu_3-C\equiv NR$); 2161 (free $C\equiv NR$) cm^{-1} .

X-ray Structure Determination. The single crystals were produced from a mixture of CH_2Cl_2 and diethyl ether. A large crystal was cut to a size $0.18 \times 0.20 \times 0.28$ mm, wedged inside a capillary tube and flame sealed. The crystal density was determined by the neutral-buoyancy method using a mixture of CCl_4 and hexane. Cell constants and an orientation matrix was determined and refined using the angular settings for 21 accurately centered high-angle reflections ($49.3 \leq 2\theta \leq 62.9^\circ$). Intensity data were recorded in ω - 2θ mode, at variable scan speeds (0.969–4.12 deg·min⁻¹) and a scan width of $0.65 + 0.14 \tan \theta$, with a maximum time per datum of 50 s.¹³ Static background measurements were made at the endpoints of the width $0.75 \pm 0.14 \tan \theta$. Three standard reflections were monitored every 120 min of X-ray exposure time, and 11 896 data were collected ($-14 \leq h \leq 14$, $-1 \leq k \leq 45$, $-14 \leq l \leq 14$; $0 \leq 2\theta \leq 110^\circ$). The NRCVAX crystal structure programs¹⁴ running on a SUN 3/80 workstation were used to process the data. Nine faces were identified

Table 2. Crystal Data and Experimental Details

compound, fw	$C_{84}H_{78}N_2F_{12}P_8Pd_3$, 1893.55
cryst syst, space group	monoclinic, $P2_1/n$
temp, °C	23
cel dimens	
<i>a</i> , Å	13.624(1)
<i>b</i> , Å	42.373(3)
<i>c</i> , Å	14.025(1)
β , deg	98.78(5)
<i>Z</i>	4
cell vol, Å ³	8001.1(8)
calcd (obsd) density, g·cm ⁻³	1.572 (1.58)
<i>F</i> (000)	3808
diffractometer, filter	Enraf Nonius CAD4F; nickel
radiation; wavelength, Å	Cu K α ; 1.54184
abs coeff, cm ⁻¹	72.4
no. of obsrvn no. of variables	5535 ($I \geq 3\sigma(I)$); 402
final model: <i>R</i> , <i>R</i> _w ^a	0.0597, 0.0641

$$^a R = \sum(|F_o| - |F_c|) / \sum|F_o|; R_w = [\sum w^{1/2}(|F_o| - |F_c|)] / \sum w^{1/2}|F_o|.$$

Table 3. Selected Atomic Positional ($\times 10^4$) and Thermal ($\times 10^3$) Parameters^a

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} , Å ²
Pd(1)	3398.0(8)	1188.0(2)	7043.2(6)	28.9(3)*
Pd(2)	2642.0(8)	1229.7(2)	8671.7(6)	29.5(3)*
Pd(3)	1598.6(8)	1391.0(2)	7020.3(7)	28.7(3)*
P(1)	4839(3)	945(1)	7755(3)	33(1)*
P(2)	3930(3)	945(1)	9618(2)	32(1)*
P(3)	1314(3)	1317(1)	9508(2)	34(1)*
P(4)	91(3)	1336(1)	7550(2)	33(1)*
P(5)	1258(3)	1500(1)	5404(2)	34(1)*
P(6)	3106(3)	1094(1)	5387(2)	34(1)*
C(10)	4660(10)	716(3)	8840(9)	35(3)
C(20)	221(9)	1503(3)	8771(8)	24(3)
C(30)	2282(10)	1397(3)	4748(9)	37(3)
C(1)	2963(11)	1609(4)	7719(10)	40(5)*
N(1)	3230(9)	1871(3)	7808(8)	41(4)*
C(11)	3461(9)	2189(3)	7688(7)	58(5)
C(12)	3350(9)	2399(3)	8426(7)	65(5)
C(13)	3518(9)	2720(3)	8310(7)	80(6)
C(14)	3796(9)	2830(3)	7456(7)	96(7)
C(15)	3907(9)	2620(3)	6717(7)	79(6)
C(16)	3739(9)	2299(3)	6833(7)	71(5)
C(17)	3071(15)	2293(4)	9369(11)	79(7)*
C(18)	3850(16)	2067(4)	6023(12)	85(8)*
C(111)	5812(8)	1235(2)	8141(7)	46(4)
C(121)	5429(7)	662(2)	7046(7)	44(4)
C(211)	4818(6)	1198(2)	10335(6)	35(3)
C(221)	3690(8)	641(2)	10473(5)	37(4)
C(311)	1659(7)	1586(2)	10511(6)	40(4)
C(321)	769(8)	990(2)	10083(8)	42(4)
C(411)	-1012(7)	1521(2)	6897(7)	25(3)
C(421)	-250(6)	928(2)	7697(6)	36(3)
C(511)	1150(8)	1921(2)	5189(5)	37(4)
C(521)	173(8)	1311(2)	4726(7)	39(4)
C(611)	4146(7)	1088(2)	4717(7)	33(3)
C(621)	2434(8)	731(2)	5015(5)	39(4)

^a All of the atomic parameters were assigned anisotropic thermal parameters given as the isotropic equivalent displacement parameter defined as $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^*$.

for the data crystal and the distances among them were measured on a microscope. A gaussian absorption correction was applied to the data using the routine "absorp". The maximum and minimum transmission values are 0.3955 and 0.2867. The space group was assigned as $P2_1/n$ on the basis of the systematic absences¹⁵ and was confirmed by successful solution and refinement of the structure. The symmetry equivalent reflections were averaged ($R_f = 0.031$, 825 pairs) accordingly, leaving 10 031 independent reflections of which 5802 were considered observed [$I \geq 2.5\sigma(I)$]. The structure was readily solved by a combination of SHELXS-86¹⁶ and difference Fourier techniques. Refinement was by full-matrix least-squares techniques on *F*, using the SHELX-76 software.¹⁷

(13) *CAD4 Diffractometer Manual*; Enraf-Nonius: Delft, The Netherlands, 1988.

(14) E. J. Gabe, Y. Le Page, J.-P. Charland and F. C. Lee, *J. Appl. Crystallogr.* **1989**, *22*, 384–387.

(15) International Tables for X-ray Crystallography: (a) D. Reidel Publishing Co.: Boston, MA 1983. Volume A. (b) Kynoch Press: Birmingham, England, 1974; Volume IV (present distributor Kluwer Academic Publishers, Dordrecht, The Netherlands).

Scattering factors for neutral, non-hydrogen atoms were taken from ref 14b. Anisotropic thermal parameters were assigned for the Pd, P, N, methyl, and isocyanide carbon atoms and were refined. The phenyl rings were constrained to regular hexagons with $d(\text{C}-\text{C})$ of 1.392 Å and their isotropic thermal parameters were refined in the least-squares cycles. All the hydrogen atoms were placed in calculated positions ($\text{C}-\text{H} = 0.95$ Å) and included in the structure factor calculations. A common thermal parameter was assigned for the hydrogen atoms and fixed at $U = 0.12$ Å². The fluorine atoms in both the PF_6^- anions were found to be disordered. The disorder components were resolved successfully, and the multiplicities were deduced from difference Fourier syntheses. The occupancy factors for the major components in each PF_6^- are 0.7 and 0.6. The anions were treated as regular octahedra with $d(\text{P}-\text{F})$ of 1.60 Å. The weighting scheme employed was of the form $w = k/\sigma^2(F_o) + gF^2$, where $k = 1.1810$

- (16) Sheldrick, G. M. SHELXS-86, Structure Solving Program. University of Gottingen, F.D.R., 1986.
- (17) Sheldrick, G. M. SHELX-76, Program for Crystal Structure Determination. University of Cambridge England, 1976.

and $g = 0.002267$. The top five peaks in the final difference Fourier synthesis are in the electron density range from 0.994 to 0.743 $\text{e}\cdot\text{Å}^{-3}$; of these, three were associated with Pd atoms, one near the C(113) atom (at a distance of 0.71 Å) and the other 1.13 Å away from F(8). The largest shift/ESD in the final cycle was -0.01 on U of F(11a). The secondary extinction coefficient was refined to $4.45(40) \times 10^{-4}$. Experimental details and selected atomic positional parameters are given in Tables 2 and 3.

Acknowledgment. We thank NSERC (Canada) for financial support, Shiraz University for granting sabbatical leave to M.R., and Dr. N. C. Payne for the X-ray and computing facilities.

Supplementary Material Available: Tables of complete atomic and positional parameters, anisotropic thermal parameters, and calculated H-atom positional parameters (5 pages). Ordering information is given on any current masthead page.