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Synthesis and Characterization of a Complete Series of $[MM'(dppm)_2(CH_3CN)_2](BF_4)_2$ Complexes (M, M′ = Ni, Pd, Pt)

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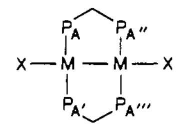
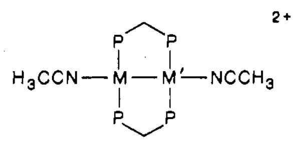
A complete series of homo- and heterobimetallic complexes of the type $[MM'(dppm)_2(CH_3CN)_2](BF_4)_2$ (M, M′ = Ni, Pd, Pt; dppm = $Ph_2PCH_2PPh_2$) have been prepared by comproportionation of appropriate M(0) and M′(II) complexes. These complexes have been characterized by ^1H and ^{31}P NMR spectroscopy. NMR evidence shows that the acetonitrile ligands are labile for all complexes containing nickel and palladium. For certain heterobimetallic complexes, a second isomer is observed involving one bridging and one chelating dppm ligand while preserving the metal–metal bond.

Introduction

Binuclear complexes of type **1** containing palladium and platinum have received considerable attention over the past 10 years.[1-8] One of the interesting features of these complexes is their ability to undergo facile reactions with a range of small molecules such as CO, SO_2, isocyanides, diazomethane, sulfur, and activated alkynes to form A-frame complexes in which small molecules are bound to both metal atoms. In this respect they can be regarded as models for metal surfaces.[1] Although the syntheses of heterobimetallic dimers of the second- and third-row metals have been described for complexes of type **1**,[9,10] no homobimetallic analogues of nickel are known nor have heterobimetallic complexes of this type that contain nickel with palladium or platinum been reported. This paper presents the synthesis and characterization of a complete series of complexes of type **2**. This series of complexes should provide an opportunity for a systematic examination of the influence of various metals on the reactivity, structure, and bonding of this class of bimetallic complexes.



1: X = Cl, Br, I, CO



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A second interesting feature of complexes of type **2** is the presence of two weakly coordinating acetonitrile ligands. In principle, these bimetallic complexes have more than one coordination site available for the binding and activation of small molecules. This feature is unusual for metal dimers and clusters, and studies of these complexes should help extend the knowledge gained by studying complexes of type **1**. The lability of both the bridging dppm ligand and the ligands trans to the Pt–Pt bond in the latter complexes has been shown to be important in substitution reactions,[11,12] A-frame formation,[13] and the oxidative addition of hydrogen.[11]

Experimental Section

General Considerations. Acetonitrile and dichloromethane were dried by distillation from calcium hydride under nitrogen. Toluene, hexanes, and diethyl ether were distilled from sodium benzophenone ketyl under nitrogen. All reactions were carried out by using standard Schlenk techniques. $Ni(COD)_2$ (COD is 1,5-cyclooctadiene) and dppm (dppm is bis(diphenylphosphino)methane) were purchased from Strem Chemicals, Inc. $Pd_2(dba)_3$ (dba is dibenzylideneacetone) was purchased from Alfa Products. $Pt(COD)_2$,[14] $[Pd(CH_3CN)_4](BF_4)_2$,[15] $[Ni(CH_3CN)_6](BF_4)_2$,[16] and $[Pt(COD)(CH_3CN)_2](BF_4)_2$[17] were prepared by literature methods. $[Ni(C_6H_5CN)_6](BF_4)_2$ was prepared in a manner strictly analogous to that used for $[Ni(CH_3CN)_6](BF_4)_2$ with use of C_6H_5CN as the solvent.

Infrared spectra were obtained on a Perkin-Elmer 599B spectrophotometer. All of the BF_4 salts showed a broad, strong infrared absorption between 900 and 1150 cm^{-1}. No bands were observed for any of the complexes in the 2100–2400-cm^{-1} range that could be assigned to coordinated acetonitrile. A JEOL FX90Q FT NMR spectrometer equipped with a tunable variable-temperature probe was used to collect ^1H and ^{31}P NMR spectra. TMS was used as an internal reference for all ^1H spectra. A capillary filled with phosphoric acid was used as an external reference for ^{31}P NMR spectra. All ^{31}P NMR spectra were proton-decoupled. Chemical shifts downfield, i.e. to the left, of the phosphoric acid resonance are assigned positive values. Initial spectral simulations were performed with the RACCOON program, a version of LAOCOON written for the IBM PC.[18] Final simulations and plotting were carried out by using the PANIC program on an Aspect 2000 computer.[19]

$[Ni(dppm)(CH_3CN)]_2(BF_4)_2$. A solution of $[Ni(CH_3CN)_6](BF_4)_2\cdot{}^1/_2CH_3CN$ (1.5 g, 3.0 mmol) in acetonitrile (50 mL) was added to a solution of bis(diphenylphosphino)methane (2.31 g, 6.0 mmol) in dichloromethane (50 mL). The resulting red solution was stirred at room temperature for 1 h; then the solvent was removed on a vacuum line to give a yellow powder. The powder was dissolved in acetonitrile (50 mL), and the resulting solution was added to a stirred suspension of $Ni(COD)_2$ (0.82 g, 3.0 mmol) in acetonitrile (20 mL). The resulting green solution was stirred for 2 h before removing the solvent on a vacuum line. The crude product was recrystallized from a mixture of dichloromethane and hexanes to give a purple solid. This solid was collected by filtration and dried in vacuo at 50 °C for 5 h. The yield was 2.85 g (85%). ^1H NMR (dichloromethane-d_2): Ph, 7.3–7.7 ppm (m); CH_2, 4.48 ppm (quintet, J = 4.5 Hz); CH_3CN, 1.27 ppm (broad s). ^{31}P NMR (dichloromethane-d_2): 1.35 ppm (s). Anal. Calcd for $C_{54}H_{50}N_2B_2F_8Ni_2P_4$: C, 56.79; H, 4.42; N, 2.45; P, 10.85. Found: C, 56.53; H, 4.47; N, 2.10; P, 10.57.

$[Ni(dppm)(C_6H_5CN)]_2(BF_4)_2$. A suspension of $Ni(COD)_2$ (0.55 g, 2.0 mmol) in benzonitrile (20 mL) was added to the reaction mixture of dppm (1.54 g, 4.0 mmol) and $[Ni(C_6H_5CN)_6](BF_4)_2$ (1.70 g, 2.0 mmol) in benzonitrile (30 mL). A dark green reaction mixture formed immediately. The solvent was removed at 60 °C in vacuo to produce a dark green solid. Recrystallization of this solid from a mixture of dichloro-

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Table I. ^{31}P NMR Data for $[MM'(dppm)_2(CH_3CN)_2](BF_4)_2$ Dimers[a,b]

complex	δ_P	$^1J_{PtP}$, Hz	$^2J_{PtP}$, Hz	$^2J_{PP}$, Hz	$^3J_{PP}$, Hz
6a (NiNi)	1.35				
6b (NiNi)	1.50				
7 (PdPd)	−5.86				
8 (PtPt)	1.2	2720	−138		60 ($P_AP_{A''}$) 32 ($P_AP_{A'''}$)
9 (NiPd)	0.0 (Ni) −7.34 (Pd)			N = 63	
11 (PdPt)	−1.5 (Pt) −6.5 (Pd)	2690	−75		54 (P_AP_B) 33 ($P_AP_{B'}$) ($J_{P_AP_A} - J_{P_BP_{B'}} = 5$)
10 (NiPt)	−24.91 (P_A) 0.56 (P_B) 2.71 (P_M) −56.3 (P_X)	2419 (PtP_A) 2897 (PtP_b) 1123 (PtP_X)	−521 (PtP_M)	374 (P_AP_B) −58 (P_AP_X) −7 (P_BP_X)	5 (P_AP_M) 60 (P_BP_M) −63 (P_MP_X)
12 (PdPt)	−31.50 (P_A) −9.33 (P_B) 3.47 (P_M) −53.7 (P_X)	2250 (PtP_A) 2579 (PtP_B) 1958 (PtP_X)	(0) (PtP_M)	396 (P_AP_B) −50 (P_AP_X) 0 (P_BP_X)	16 (P_AP_M) 39 (P_BP_M) −52 (P_MP_X)

[a] See structures **1**, **9**, **10**, **11**, and **12** of the text for labeling of phosphorus atoms. [b] The relative signs of the coupling constants given in this table are the ones that give the best fit in our hands. However, they may not be unique.

methane and hexanes produced a purple solid, which was collected by filtration and dried in vacuo at 50 °C for 5 h. The yield was 1.83 g (72%). ^{1}H NMR (dichloromethane-d_2): Ph, 6.7–7.7 ppm (m); CH_2, 4.60 ppm (quintet, J = 4.5 Hz). ^{31}P NMR (dichloromethane-d_2): 1.50 ppm (s). Anal. Calcd for $C_{64}H_{54}N_2B_2F_8Ni_2P_4$: C, 60.46; H, 4.31; N, 2.21; P, 9.78. Found: C, 60.71; H, 4.40; N, 2.12; P, 9.57.

[Pd(dppm)(CH$_3$CN)]$_2$(BF$_4$)$_2$. A yellow solution of $[Pd(CH_3CN)_4](BF_4)_2$ (0.44 g, 1.0 mmol) in acetonitrile (30 mL) was added to a solution of dppm (0.77 g, 2.0 mmol) in dichloromethane (20 mL). The reaction mixture was stirred for 1 h to produce a white suspension. $Pd_2(dba)_3$ (0.50 g, 5.0 mmol) was added to the suspension, and the reaction mixture was stirred overnight. The resulting orange solution was filtered, and the solvent was removed from the filtrate with a vacuum line to produce an orange solid. The crude product was recrystallized from a mixture of dichloromethane and hexanes at −20 °C to yield 1.02 g (83%) of a yellow microcrystalline solid. The product was dried at 50 °C for 2 h in vacuo. ^{1}H NMR (dichloromethane-d_2): Ph, 7.4 ppm (m); CH_2, 5.38 ppm (quintet, J = 5 Hz); CH_3CN, 1.35 ppm (s). ^{31}P NMR (acetonitrile-d_3): −5.86 ppm (s). Anal. Calcd for $C_{54}H_{50}N_2B_2F_8P_4Pd_2$: C, 52.42; H, 4.08; N, 2.26; P, 10.01; Pd, 17.20. Found: C, 52.54; H, 4.12; N, 2.18; P, 9.81; Pd, 16.84.

[Pt(dppm)(CH$_3$CN)]$_2$(BF$_4$)$_2$. A mixture of $[Pt(COD)(CH_3CN)_2](BF_4)_2$ (0.27 g, 0.48 mmol) and $Pt(COD)_2$ (0.21 g, 0.50 mmol) in acetonitrile (50 mL) was stirred for 0.5 h to give a clear orange solution. A solution of dppm (0.38 g, 1.0 mmol) in acetone (30 mL) was added to the orange solution. The resulting reaction mixture was stirred for 1 h at room temperature and then heated to 70 °C for 60 h. The clear, red-brown solution was filtered, and the volume of the filtrate was reduced to approximately 15 mL in vacuo. Diethyl ether was added slowly to the solution to give a yellow precipitate, which was collected by filtration and dried in vacuo at 50 °C for 2 h. The yield was 0.275 g (45%). ^{1}H NMR (dichloromethane-d_2): Ph, 7.4 ppm (m); CH_2, 4.60 ppm (quintet, J = 4.5 Hz; ^{195}Pt satellites, J = 59 Hz); CH_3CN, 1.21 ppm (s; ^{195}Pt satellites, J = 8 Hz). ^{31}P NMR (dichloromethane-d_2): 1.2 ppm (s); ^{195}Pt satellite spectrum, A_4X spin system, $^1J_{PtP}$ = 2720 Hz, $^2J_{PtP}$ = −138 Hz. Anal. Calcd for $C_{54}H_{50}N_2B_2F_8P_4Pt_2$: C, 45.84; H, 3.57; N, 1.98. Found: C, 45.27; H, 3.65; N, 1.89.

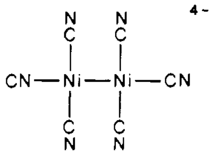
[PdNi(dppm)$_2$(CH$_3$CN)$_2$](BF$_4$)$_2$·$^1/_2$CH$_3$CN. A mixture of $[Pd(CH_3CN)_4](BF_4)_2$ (0.44 g, 1.0 mmol) and dppm (0.77 g, 2.0 mmol) in acetonitrile (50 mL) was stirred for 0.5 h to form a white suspension. $Ni(COD)_2$ (0.28 g, 1.0 mmol) was added to the suspension, and the resulting reaction mixture was stirred for an additional 2 h to produce a red-brown solution. The solution was filtered, and the solvent was removed from the filtrate on a vacuum line to produce an orange solid. This solid was recrystallized from a mixture of acetonitrile and diethyl ether. The product was collected on a frit and dried in vacuo at 50 °C for 2 h. The yield was 0.61 g (51%). ^{1}H NMR (acetone-d_6): Ph, 7.2–7.6 ppm (m); CH_2, 4.87 ppm (quintet, J = 5 Hz); CH_3CN (−92 °C), 1.36 (s) and 1.71 ppm (s). ^{31}P NMR (dichloromethane-d_2): AA′XX′ spectrum consisting of two triplets centered at −7.34 and 0.0 ppm (triplet splitting 32 Hz). Anal. Calcd for $C_{55}H_{51.5}N_{2.5}B_2F_8P_4NiPd$: C, 54.58; H, 4.29; N, 2.89. Found: C, 52.32; H, 4.41; N, 2.91.

[PtNi(dppm)$_2$(CH$_3$CN)$_2$](BF$_4$)$_2$. A suspension of $[Pt(dppm)_2](BF_4)_2$ (0.50 g, 0.44 mmol) and $Ni(COD)_2$ (0.12 g, 0.44 mmol) in acetonitrile (30 mL) was stirred for 2 h to form a clear red solution. The solution was filtered and the solvent removed from the filtrate in vacuo to produce a red-brown solid. This product was recrystallized from a mixture of acetonitrile and diethyl ether, collected by filtration, and dried on a vacuum line at 50 °C for 2 h. The yield was 0.47 g (84%). ^{1}H NMR (dichloromethane-d_2): Ph, 7.4 ppm (m); CH_2, 4.50 (m); CH_3CN, 1.69 (s). ^{31}P NMR (dichloromethane-d_2): complex second-order pattern that can be simulated by using the parameters listed in Table I. Anal. Calcd for $C_{54}H_{50}N_2B_2F_8NiP_4Pt$: C, 50.73; H, 3.95; N, 2.19. Found: C, 50.51; H, 4.11; N, 1.44.

[PdPt(dppm)$_2$(CH$_3$CN)$_2$](BF$_4$)$_2$. $Pt(COD)_2$ (0.21 g, 0.5 mmol) was added to a suspension of $[Pd(dppm)_2](BF_4)_2$ (0.52 g, 0.5 mmol) in acetonitrile (50 mL). The resulting reaction mixture was stirred for 2 h to give a clear, red solution. The solution was filtered, and the solvent was removed from the filtrate on a vacuum line. The resulting red-brown solid was recrystallized from a mixture of acetonitrile and toluene at −20 °C. The product was collected by filtration and dried in vacuo at 50 °C for 2 h. The yield was 0.295 g (44%). ^{1}H NMR (dichloromethane-d_2): Ph, 7.45 ppm (m); CH_2, 4.51 ppm (m); CH_3CN, 1.18 ppm (t, $^4J_{PtH}$ = 7 Hz) and 1.58 ppm. ^{31}P NMR (dichloromethane-d_2): complex second-order spectrum that can be simulated by using the parameters listed in Table I. Anal. Calcd for $C_{54}H_{50}N_2B_2F_8P_4PdPt$: C, 48.92; H, 3.80; P, 9.34. Found: C, 48.72; H, 3.89; P, 9.05.

Results and Interpretations

Although Pd and Pt dimers of type **1** are well-known, we know of no examples of analogous Ni dimers. This is surprising in view of the fact that the Ni(I) dimer **3** has been known for some time.[20]



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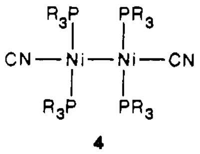

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In addition, the electrochemical reductions of nickel(II) cyano phosphine complexes such as $[Ni(CN)_2(PEt_2Ph)_2]$ result in formation of unstable complexes similar to **4**.[21] The nickel(I) dimer $[Ni_2(\mu\text{-}CNMe)(CNMe)_3(dppm)_2](PF_6)_2$ (**5**) was synthesized recently by comproportionation of $[Ni(CNMe)_4](PF_6)_2$ and $Ni(CNMe)_4$ followed by reaction with dppm.[22] Complexes **3**–**5** all contain either cyanide or isocyanide ligands in positions trans to the Ni–Ni bond. It was of interest to determine if stable nickel(I) dimers could be synthesized without this particular structural feature.

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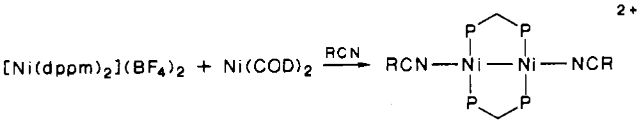
The reaction of $Ni(COD)_2$ (where COD is 1,5-cyclooctadiene) with $[Ni(dppm)_2](BF_4)_2$ in acetonitrile followed by recrystallization from a mixture of dichloromethane and hexanes results in the formation of $[Ni(dppm)(CH_3CN)]_2(BF_4)_2$ (**6a**), as shown in eq 1. The analogous benzonitrile complex, **6b**, can be prepared by changing the solvent from acetonitrile to benzonitrile. The products are isolated as deep purple solids, which are moderately air sensitive in the solid state and in solution.



6a, R = CH_3
b, R = C_6H_5 (1)

In dichloromethane, both complexes exhibit a sharp single resonance in the ^{31}P NMR spectrum as expected since all phosphorus atoms are chemically equivalent. The chemical shifts of 1.35 and 1.50 ppm for complexes **6a** and **6b**, respectively, are consistent with a bridging dppm ligand.[21] When dppm chelates to a single metal to form a four-membered ring, the resonance for the phosphorus atoms occurs at much higher fields.[23,24] For example, $[Ni(dppm)_2](BF_4)_2$, which has two chelating dppm ligands, has a single resonance at −35.4 ppm. Evidence for the presence of four phosphorus atoms in these complexes is the observation of a quintet for the methylene protons of the bridging dppm ligand.[23,24] This pattern arises from the coupling of the methylene protons to the four strongly coupled phosphorus atoms.

The presence of coordinated acetonitrile in **6a** is indicated by the observation of a methyl resonance at 1.27 ppm in dichloromethane-d_2 at −70 °C. At room temperature, this resonance is broad. This is consistent with a rapid reversible dissociation of acetonitrile. If acetonitrile is added to the NMR sample at room temperature, the resonance assigned to acetonitrile increases in intensity and shifts toward the position of free acetonitrile. The elemental analyses are also consistent with the presence of two acetonitrile or benzonitrile ligands per molecule. However, no IR bands are present in the 2100–2400-cm^{-1} range expected for coordinated acetonitrile or benzonitrile ligands for **6a** and **6b** or for any of the complexes described in this paper. Apparently, the intensity of this band is to weak to be detected for this class of compounds.

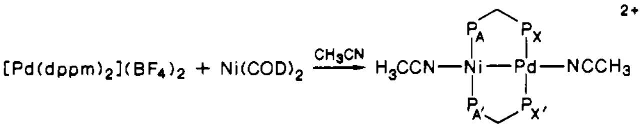
Reaction of $[Pd_2(dba)_3]$ (where dba is dibenzylideneacetone) with $[Pd(dppm)_2](BF_4)_2$ in acetonitrile results in the formation of $[Pd(dppm)(CH_3CN)]_2(BF_4)_2$ (**7**). This orange-brown complex is moderately air-sensitive. The observation of a single resonance in the ^{31}P NMR spectrum of this compound with a chemical shift of −5.86 ppm is indicative of a bridging dppm ligand. The resonance assigned to the methylene protons of the bridging dppm ligand is a quintet at 5.38 ppm with a splitting of 5 Hz. This observation is again consistent with the coupling of these protons to four strongly coupled phosphorus atoms. A sharp methyl resonance assigned to coordinated acetonitrile is observed at 1.35 ppm when dichloromethane-d_2 is used as the solvent. On addition of acetonitrile to this solution, this resonance broadens and shifts toward the position of free acetonitrile. In acetonitrile-d_3 solutions, the resonance for acetonitrile occurs at the position of free acetonitrile. These observations indicate that the acetonitrile ligands in this complex are also labile.

Under conditions strictly analogous to those used for the preparation of the nickel and palladium dimers, no reaction was observed between $Pt(COD)_2$ and $[Pt(dppm)_2](BF_4)_2$. Refluxing the reaction mixture in acetonitrile for 3 weeks resulted in the formation of impure product in very low yields. To circumvent these difficulties, a different preparative route was used. It seemed reasonable that replacement of the chelating dppm ligands of $[Pt(dppm)_2](BF_4)_2$ with ligands that were more labile might facilitate the initial formation of the Pt–Pt bond. This appears to be the case since reaction of $Pt(COD)_2$ with $[Pt(COD)(CH_3CN)_2](BF_4)_2$ followed by treatment with dppm gives $[Pt(dppm)(CH_3CN)]_2(BF_4)_2$ (**8**) in reasonable yields and high purity.

The ^{31}P NMR spectrum of $[Pt(dppm)(CH_3CN)]_2(BF_4)_2$ consists of a single resonance at 1.2 ppm with A_4X and A_4X_2 satellite spectra arising from isotopomers containing one and two ^{195}Pt isotopes, respectively. The appearance and analysis of the spectrum are very similar to those of $[Pt(dppm)Cl]_2$,[24] and the analysis is not repeated here. The parameters derived from such an analysis are given in Table I. In addition, the observation of resonances assignable to the A_4X_2 isotopomer allows an estimation of the PtPt coupling constant to be made. The value obtained from spectral simulation is 7200 Hz, which is similar to the value of 10 269 Hz observed for $[Pt(Ph_2Ppy)Cl]_2$ (Ph_2Ppy is 2-(diphenylphosphino)pyridine).[9]

The methylene protons of dppm appear as a quintet in the ^1H NMR spectrum due to coupling with the four phosphorus atoms of the complex. Satellites are also observed for the methylene protons due to coupling to ^{195}Pt. The magnitude of the PH coupling and PtH coupling are appropriate for a dimeric complex.[24] In dichloromethane-d_2, the methyl resonance for coordinated acetonitrile is observed at 1.21 ppm with shoulders arising from coupling to Pt ($^4J_{PtH}$ = 8 Hz). This resonance is unaffected by the addition of acetonitrile to the NMR sample. These observations indicate that the acetonitrile ligands are not as labile for the homobimetallic platinum dimer as they are for the analogous nickel and palladium complexes, in which they exchange with free acetonitrile to at least −50 °C.

The heterobimetallic dimers can be prepared in a straightforward manner by the comproportionation reactions 2–4. These reactions are surprisingly clean and do not give a statistical distribution of products. The isolated heterobimetallic complexes do not cleave to give mixtures of homobimetallic dimers, and mixtures of the homobimetallic dimers are stable under conditions similar to those used to prepare the dimers. These observations indicate that formation of the metal–metal bonds in reactions 2–4 are determined by the kinetics of these reactions and not by thermodynamics. The arrangements of the remaining ligands about the metal–metal axes appear to be under thermodynamic control. For example, complex **10** is also formed when $Pt(COD)_2$ is reacted with $[Ni(dppm)_2](BF_4)_2$, which requires cleavage of nickel–phosphorus bonds and formation of platinum–phosphorus bonds.



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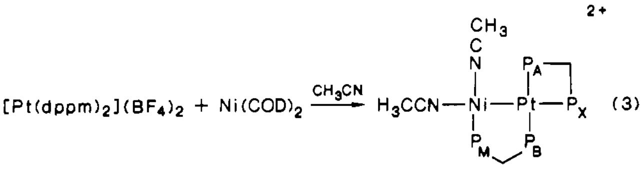

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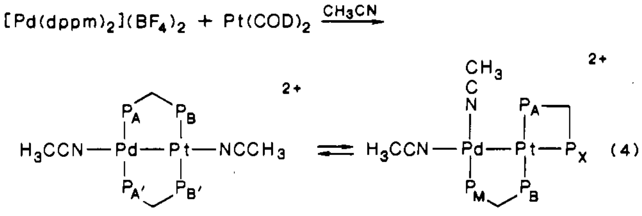

11 **12**

The ^{31}P NMR spectrum of **9** consists of two triplets centered at −7.3 and 0.0 ppm. The chemical shift values for these two triplets agree well with those of the palladium dimer (−5.9 ppm)

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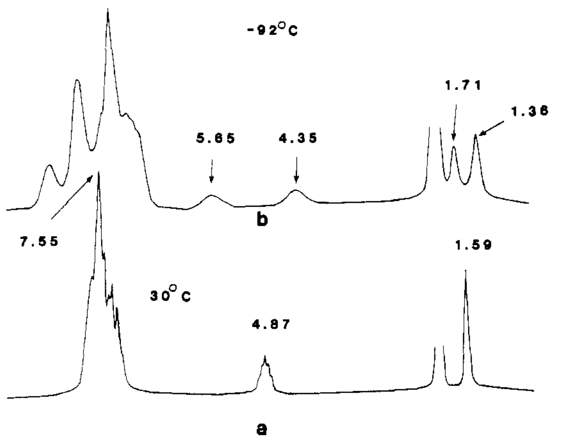

Figure 1. ^1H NMR spectra of $[NiPd(dppm)_2(CH_3CN)_2](BF_4)_2$ in acetone-d_6 at (a) 30 °C and (b) -92 °C. Chemical shifts of selected resonances are indicated by arrows.

and the nickel dimer (+1.35 ppm). On the basis of these data the triplet resonance at 0.0 ppm is assigned to the phosphorus atoms coordinated to nickel and the resonance at -7.3 ppm is assigned to the phosphorus atoms coordinated to palladium. In addition, the resonances centered at 0.0 ppm are broader than those centered at -7.3 ppm. In the homobimetallic dimers the singlet for the Ni dimer is broader than that of the palladium dimer. Since large phosphorus-phosphorus coupling constants are observed in the mixed palladium-platinum dimers and the nickel-platinum dimer, as discussed below, this spectrum is best interpreted as a deceptively simple AA'XX' spectrum. The only parameters that can be obtained with any confidence from the spectrum are the chemical shift difference and N (63 Hz), which is $J_{AX} + J_{AX'}$ in **9**.[25] This value is similar to those observed for $J_{AM} + J_{BM}$ in **10** and **12** (Table I).

The proton NMR spectrum exhibits an apparent quintet for the methylene protons of dppm at 4.87 ppm at room temperature with a splitting of 5 Hz. Again the quintet pattern and the phosphorus chemical shifts are diagnostic of a dimeric structure for this complex. At -92 °C in acetone-d_6 two resonances are observed at 1.71 and 1.36 ppm as shown in Figure 1. These resonances are assigned to the two acetonitrile ligands coordinated to nickel and palladium. It is not possible by using the data at hand to make an unambiguous assignment of which resonance corresponds to the acetonitrile ligand coordinated to nickel or palladium. When the sample is warmed, the two methyl resonances coalesce at -70 °C and appear as a single resonance above -65 °C. These results indicate that the acetonitrile ligands exchange rapidly. After addition of acetonitrile to the NMR sample at -96 °C, the resonance at 1.36 ppm is not observed due to rapid exchange with free acetonitrile while the resonance at 1.71 ppm is unaffected. This result shows that the acetonitrile ligand associated with the resonance at 1.36 ppm is still exchanging rapidly with free acetonitrile at this temperature while the other acetonitrile ligand is not. A second exchange process is observed for the methylene protons of the coordinated dppm ligand. As shown in Figure 1, the methylene resonance for dppm appears as a quintet centered at 4.87 ppm at room temperature. At -92 °C two broad resonances are observed at 5.65 and 4.35 ppm. These resonances coalesce at -26 °C, which gives an activation barrier for this process of 12 kcal/mol.[26] Presumably the two resonances observed at -92 °C are associated with axial and equatorial hydrogens of the "six-membered" ring, as described previously for $[Pt(dppm)(PPh_3)]_2^{2+}$.[27] The resonances in the phenyl region of the ^1H NMR spectrum are also significantly altered over the temperature range in which resonances for the methylene protons of dppm show temperature dependence. The appearance of the ^{31}P NMR spectrum is unchanged throughout this temperature range.

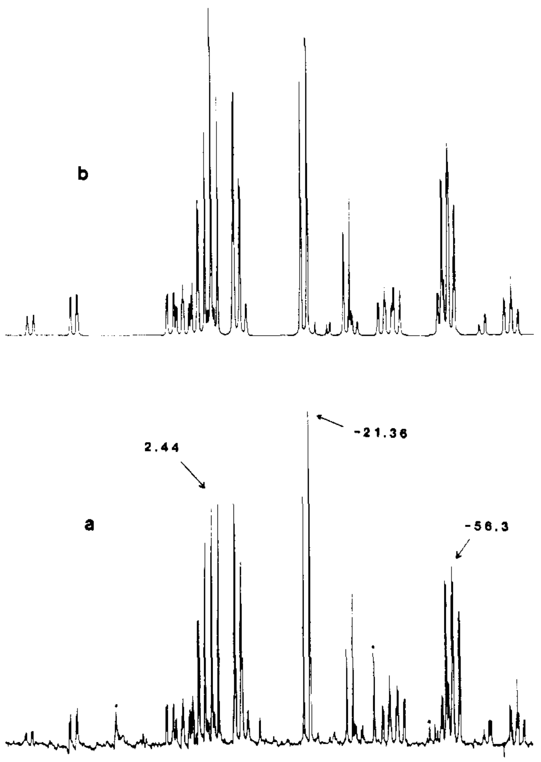

Figure 2. (a) Experimental ^{31}P NMR spectrum of $[NiPt(dppm)_2(CH_3CN)_2](BF_4)_2$ in acetonitrile-d_3. (b) Simulated spectrum with use of parameters given in Table I. Asterisks indicate impurities. Chemical shifts of selected resonances are indicated by arrows.

The ^{31}P NMR spectrum of **10** is quite complex and is shown in Figure 2 together with the simulated spectrum for this complex. This spectrum can be understood as an ABMX spectrum with ^{195}Pt satellite spectra. This spin system is consistent with structure **10** and not with the more symmetrical structure observed for the nickel-palladium dimer. Complexes containing both bridging and chelating dppm ligands have been reported previously. $[Pt_2(dppm)_3]^{2+}$ has been characterized by an X-ray structure,[28] and $[Pt_2(dppm)_2(PPh_3)I]^+$ has been detected as a reaction intermediate and characterized by ^{31}P NMR.[12] It is somewhat surprising that the chelating diphosphine in **10** is bound to platinum rather than nickel since the ring strain for the four-membered ring would be expected to be smaller for the smaller nickel atom. However, the magnitudes of the PtP coupling constants (see Table I) clearly indicate that the chelating diphosphine is bound to platinum. The values of the remaining coupling constants are consistent with those observed for related complexes.[3,12]

The ^1H NMR spectrum of **10** in dichloromethane-d_2 at room temperature exhibits a single broad resonance at 1.69 ppm assigned to coordinated acetonitrile and a multiplet for the methylene protons of the bridging and chelating dppm ligands. When the sample is cooled to -90 °C, two resonances are observed for the acetonitrile ligands at 1.59 and 1.46 ppm. Addition of acetonitrile at -90 °C results in a shifting of the resonance at 1.46 ppm to that of free acetonitrile while the resonance at 1.59 ppm remains unchanged. Whether it is the acetonitrile ligand that is trans to phoshorus or platinum that is more labile is ambiguous on the basis of the spectral data, but clearly one site is more labile than the other. Since platinum has a larger trans influence than phosphorus,[29] one might suspect that it is acetonitrile trans to platinum which is more labile.

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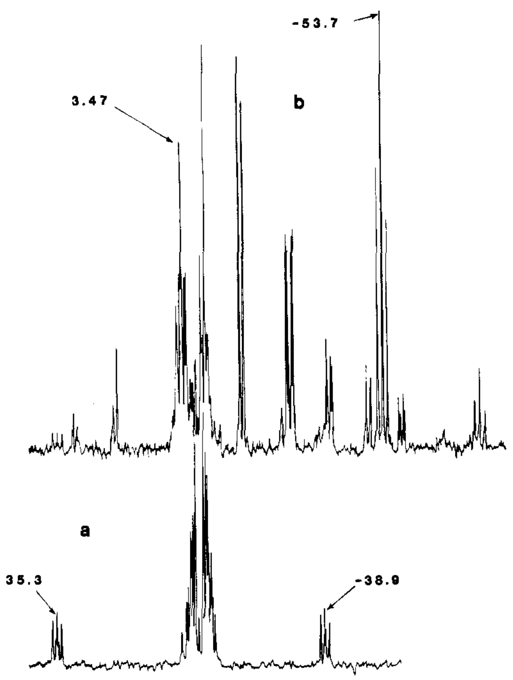

Figure 3. ^{31}P NMR spectra: (a) isomer **11** in acetonitrile; (b) isomer **12** in acetone. Chemical shifts of selected resonances are indicated by arrows.

The geometry adopted by the palladium–platinum dimer is solvent-dependent. In acetonitrile the more symmetrical isomer **11** is the predominant species in solution as shown by the ^{31}P NMR spectrum (Figure 3a). This spectrum is clearly that of an AA'XX' spin system with platinum satellites and can be simulated by using the parameters given in Table I. These parameters are consistent with those observed for $[PdPt(dppm)_2Cl_2]$.[10] In acetone the isomer that predominates at equilibrium is the less symmetrical dimer **12**, in which a chelating diphosphine ligand is bound to platinum. The spectrum of this isomer is shown in Figure 3b. In dichloromethane solutions ^{31}P NMR spectra indicate that isomers **11** and **12** are present in approximately a 2:1 ratio. The spectrum shown in Figure 3b is consistent with an ABMX spin system with ^{195}Pt satellite spectra, as discussed above for the Ni–Pt dimer. The parameters used to simulate this spectrum are given in Table I. These values are similar to those observed for the Ni–Pt dimer.

The proton NMR spectrum of a mixture of **11** and **12** in dichloromethane-d_2 at 30 °C exhibits a singlet at 1.18 ppm with ^{195}Pt satellites ($^4J_{PtH}$ = 7 Hz). This resonance is assigned to the acetonitrile ligand coordinated to platinum of isomer **11**. A second broad resonance at 1.58 ppm is assigned to the rapidly exchanging acetonitrile ligands coordinated to palladium of both isomers. A multiplet is observed at 4.51 ppm for the bridging methylene protons, and the signal has ^{195}Pt satellites ($^3J_{PtH}$ = 68 Hz). When the sample is cooled to −52 °C, the resonance at 1.58 ppm splits into three resonances at 1.64, 1.59, and 1.31 ppm with relative intensities of approximately 1:1:2. The resonance at 1.31 ppm is assigned to the acetonitrile ligand coordinated to the palladium atom of isomer **11** since the intensity of this resonance is equivalent to that of the resonance at 1.18 ppm assigned to the acetonitrile bound to platinum. The remaining two resonances are assigned to the acetonitrile ligands coordinated to palladium of isomer **12**. Addition of acetonitrile to the NMR sample at −70 °C results in a shift of the resonance at 1.59 ppm to coincide with the resonance for free acetonitrile, and the resonance at 1.31 ppm is broadened. This result is consistent with the rate of exchange of acetonitrile for the various resonances being $1.59 > 1.31 > 1.64 \gg 1.18$ ppm. Since the trans influence of Pt is reported to be greater than that of phosphorus,[29] the resonance at 1.59 ppm can tentatively be assigned to the acetonitrile ligand trans to platinum in isomer **12** and the resonance at 1.64 ppm to the acetonitrile trans to phosphorus. This assignment would be consistent with the acetonitrile ligands trans to platinum in both isomers exchanging faster than the acetonitrile ligand trans to phosphorus.

Discussion and Summary

A general method has been found for the synthesis of a complete series of homo- and heterobimetallic compounds of nickel, palladium, and platinum. ^{31}P NMR studies show that the homobimetallic dimers all have symmetrical structures such as **6**. For the heterobimetallic compounds two structural types have been observed. For the nickel–palladium dimer only the symmetrical structure **9** containing two bridging dppm ligands is observed. The nickel–platinum dimer exhibits only the unsymmetrical structure **10** containing one bridging and one chelating dppm ligand. The palladium–platinum dimer exhibits either or both structures depending on the solvent. It seems likely that ring strain would favor the symmetrical structures since two five-membered rings are formed in this structure as opposed to one four-membered ring and one five-membered ring for the unsymmetrical dimers. In addition, it would seem likely that ring strain would be highest for those unsymmetrical dimers in which the four-membered rings involved the largest metal atom. However, whenever the unsymmetrical dimers are formed, the largest metal atom, platinum, is part of the four-membered ring. The observed results are the opposite of what is expected on the basis of these qualitative ring strain arguments. An alternative explanation for the observed structures is that the order of metal–phosphorus bond strength is Pt > Pd > Ni. In this case the unsymmetrical dimers are favored by the formation of the maximum number of strong metal–phosphorus bonds and the symmetrical dimers are favored by ring strain. Consistent with this interpretation is the observation that addition of trimethyl phosphite to an NMR tube containing the unsymmetrical nickel–platinum dimer results in the formation of a symmetrical dimer. A similar rearrangement occurs when bridging ligands such as carbon monoxide or acetylene[30] are added to **10**.

The ability of dppm to bridge two metals or chelate to a single metal in this class of dimers leads to three structural types that are bridged by two, one, or no dppm ligand. These dimers have different dihedral angles between the two planes defined by the three ligands bound to each metal atom. This angle has a value of 33–40° in dimers with two bridging dppm ligands.[6,11,27,31] It is much larger for the structurally characterized dimer $[Pt_2(dppm)_3]^{2+}$ (59°), which has a single bridging dppm ligand.[28] Dimers that have no bridging ligands exhibit angles of 60–90°, and free rotation about the metal–metal bond is possible.[20,31] With these structural features in mind, it is of interest to compare single-bond PtP coupling constants, $^1J_{PtP}$, for the phosphorus atoms trans to nickel, palladium, and platinum in unsymmetrical dimers such as **10** and **12**. Comparisons of $^1J_{PtP}$ for platinum dimers containing two bridging dppm ligands and for square-planar Pt(II) complexes have been used to construct a trans-influence series of H $\simeq$ Pt > P > Cl.[29] The single-bond couplings of Pt to the phosphorus atom trans to nickel and palladium of **10** and **12** are 1123 and 1958 Hz, respectively. For the related platinum dimer $[Pt_2(dppm)_2(PPh_3)I]^+$ the $^1J_{PtP}$ coupling constant is 1607 Hz.[12] With use of these values, a tentative trans-influence series can be constructed: Ni > Pt > Pd. Clearly, more results on isostructural compounds are needed before much confidence can be placed in such a series. In the proposal of this series data from the more common dimers with two bridging dppm ligands have not been used since it is not known if coupling constants in these systems are dependent on the dihedral angle discussed above.

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Another interesting feature of these dimers is the lability of the acetonitrile ligands. From our qualitative results the rate of exchange is Ni ≃ Pd ≫ Pt. This is the same order expected for ligand exchange of square-planar complexes in the +2 oxidation state.[33] Parallels between square-planar d^8 complexes and d^9–d^9 dimers have been noted previously.[29] This order also seems to coincide qualitatively with the rates of reactions of these dimers with small molecules such as hydrogen and acetylene.[30]

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Registry No. **6a**, 114718-99-9; **6b**, 114692-89-6; **7**, 109637-10-7; **8**, 114692-91-0; **9**, 114692-93-2; **10**, 114692-97-6; **11**, 114692-95-4; **12**, 114692-99-8; $[Ni(C_6H_5CN)_6](BF_4)_2$, 114693-00-4; $[Pt(COD)(CH_3CN)_2](BF_4)_2$, 66347-86-2; $[Ni(CH_3CN)_6](BF_4)_2$, 15170-11-3; $Ni(COD)_2$, 1295-35-8; $[Pd(CH_3CN)_4](BF_4)_2$, 21797-13-7; $Pd_2(dba)_3$, 51364-51-3; $Pd(COD)_2$, 12130-66-4; Ni, 7440-02-0; Pd, 7440-05-3; Pt, 7440-06-4.

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Kinetics and Mechanism of the Outer-Sphere Electron-Transfer-Induced Formation of *cis*-Dioxovanadium(V) Species from Vanadyl(IV) Complexes. Crystal Structures of $[VO(TCDA)]\cdot H_2O$ and $[VO_2(TCDAH)]\cdot 2H_2O$ (TCDA = 1,4,7-Triazacyclononane-*N,N'*-diacetate)

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The potentially pentadentate ligands 1,4,7-triazacyclononane-*N,N'*-diacetate ($C_{10}H_{17}N_3O_4^{2-}$, TCDA) and 1-oxa-4,7-diazacyclononane-*N,N'*-diacetate ($C_{10}H_{16}N_2O_5^{2-}$, DOCDA) have been synthesized, and the corresponding blue vanadyl(IV) complexes $[VO(TCDA)]\cdot H_2O$ (**1**) and [VO(DOCDA)] have been isolated. Oxidation of **1** in 0.1 M H_2SO_4 with PbO_2 or $[Ni([9]aneN_3)_2]^{3+}$ ($[9]aneN_3$ = 1,4,7-triazacyclononane) yields yellow $[VO_2(TCDAH)]\cdot 2H_2O$ (**2**). The crystal structures of **1** and **2** have been determined by X-ray crystallography. Crystal data for **1**: monoclinic, space group $P2_1/c$; $a = 6.679$ (2), $b = 10.323$ (3), $c = 18.701$ (5) Å; $\beta = 90.85$ (2)°; $V = 1289.2$ (5) Å^3, $Z = 4$, $\rho_{calcd} = 1.70$ g cm^{-3}; final $R = 0.036$ from 3383 observed reflections. Crystal data for **2**: monoclinic, space group $P2_1/n$; $a = 13.361$ (8), $b = 15.533$ (5), $c = 15.986$ (8) Å; $\beta = 111.77$ (4)°; $V = 3039.4$ (8) Å^3; $Z = 8$; $\rho_{calcd} = 1.59$ g cm^{-3}; final $R = 0.044$ from 4937 observed reflections. Cyclic voltammograms of **1** and [VO(DOCDA)] in acetonitrile show one reversible one-electron-transfer process ($VO^{2+} \rightleftarrows VO^{3+} + e^-$) at $E_{1/2} = +0.427$ and $+0.622$ V vs Fc^+/Fc, respectively. The kinetics of the acid-independent outer-sphere one-electron oxidation of **1** and [VO(DOCDA)] with $[Ni([9]aneN_3)_2]^{3+}$ as one-electron oxidant has been measured in acidic aqueous solution ($k_{12} = 685$ M^{-1} s^{-1} for **1** and 14 M^{-1} s^{-1} for [VO(DOCDA)] at 25 °C, $I = 0.56$ M). This reactivity difference is discussed in the frame of the Marcus cross relation for outer-sphere electron-transfer processes.

Introduction

Oxovanadium(IV) complexes of amino polycarboxylates are readily oxidized in acidic aqueous solution by strong outer-sphere one-electron oxidants such as $[IrCl_6]^{2-}$ or $[(en)_4Co^{III}_2(\mu\text{-}NH_2,O_2^-)]^{4+}$ to form *cis*-dioxovanadium(V) species. Sasaki, Saito, and co-workers have in a series of elegant kinetic studies proposed that oxovanadium(V) species are probable intermediates.[2-4] They have used aquaoxo(quadridentate)vanadium(IV) complexes (quadridentate = amino polycarboxylato ligands) as starting materials, where the aqua ligand is cis with respect to the V=O group. Upon deprotonation of this aqua group (OV^{IV}—OH), oxidation, and subsequent further deprotonation the *cis*-dioxovanadium(V) species are generated:

$$[OV^{IV}(OH_2)L]^n \overset{K_a}{\rightleftarrows} [OV^{IV}(OH)L]^{n-1} + H^+ \tag{1}$$

$$[OV^{IV}(OH)L]^{n-1} + \text{oxidant} \rightarrow [OV^{V}(OH)L]^n + \text{reduced oxidant} \tag{2}$$

$$[OV^{V}(OH)L]^n \rightarrow [O_2V^{V}L]^{n-1} + H^+ \tag{3}$$

In the case of $Na[V^{IV}O(edtaH)]$ (edtaH = monoprotonated ethylenediaminetetraacetate), a six-coordinate vanadyl(IV) complex with no aqua ligand but a pentadentate edta ligand instead, the presence of a steady-state oxovanadium(V)–edta complex has been detected.[4] The final oxidation product was again a *cis*-dioxovanadium(V)–edta complex, where the edta ligand is only tetradentate.[10]

Pseudooctahedral oxovanadium(IV)[5-7] and *cis*-dioxovanadium(V)[8-10] amino polycarboxylato complexes have been characterized by X-ray crystallography as have been a few five- and six-coordinate monooxovanadium(V) complexes with Schiff-base ligands.[11,12] Electrochemical data on $[VOL]^n \rightleftarrows [VOL]^{n+1} + e^-$ systems are extremely rare.

At the outset of this work we hoped to be able to characterize the proposed oxovanadium(V) intermediates by oxidizing oxovanadium(IV) compounds that contain a strongly binding pentadentate chelate ligand which might inhibit the rapid formation of *cis*-dioxovanadium(V) species in aqueous solution. For this purpose we have synthesized two new, potentially pentadentate amino polycarboxylate ligands, namely 1,4,7-triazacyclononane-*N,N'*-diacetate (TCDA) and 1-oxa-4,7-diazacyclononane-*N,N'*-diacetate (DOCDA), via functionalization of the parent cyclononanes.[13] Both ligands readily form the corresponding six-co-

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