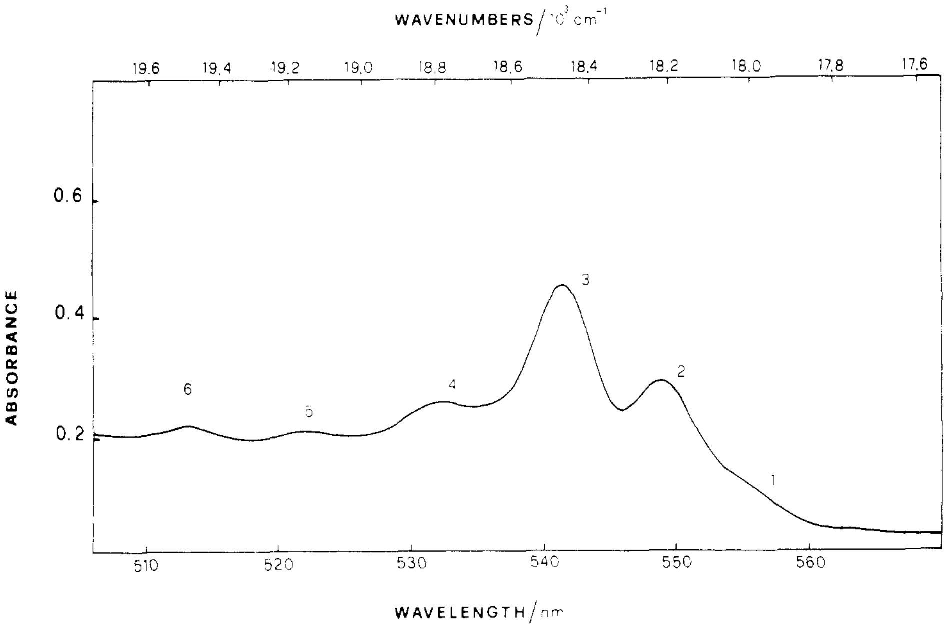

Figure 1. Cooperative absorptions for a K_2TcCl_6 crystal (1.0 mm thick) at 9 K.

and Cs_2ReCl_6, this group of bands centered at 18 500 cm^{-1} is readily assigned as cooperative absorptions.[12] Their energies can be expressed as the sums of the energies of the electronic $\Gamma_8(^2E_g)$, $\Gamma_8(^2T_{1g})$, and $\Gamma_6(^2T_{1g})$ states (Table I), but the difference between the experimental and the calculated positions is bigger than that for the pure hexachlororhenate compounds. Neither progressions in the ν_1 mode nor vibronic origins are observed. This behavior differs from that observed for K_2ReCl_6 and Cs_2ReCl_6, for which the first members of the progressions in the ν_1 mode on the cooperative absorptions are easily measurable.

The total oscillator strength of the band system centered at 18 500 cm^{-1} was calculated on the basis of single $TcCl_6{}^{2-}$ ions, although the transitions involve a two-center electronic excitation, and is $\approx 3 \times 10^{-6}$. The total relative intensities of the cooperative absorptions, referred to the neighboring transitions (origins plus vibronic sidebands) to the $\Gamma_7(^2T_{2g})$ and $\Gamma_8(^2T_{2g})$ states and evaluated by graphical methods (±10% precision), are identical ($\approx$17%) for K_2ReCl_6 (paramagnetic phase) and K_2TcCl_6. The large line width of the cooperative absorptions, already observed for the pure hexachlororhenates, is explained as the result of the combination of all the broadening mechanisms of the single ion transitions.

All of the six possible simultaneous excitations are observed for K_2TcCl_6, and no cooperative absorption is obscured by overlapping single ion transitions. Conversely, the transition to the $\Gamma_8(^2E_g) + \Gamma_8(^2E_g)$ state cannot be measured for K_2ReCl_6 and Cs_2ReCl_6, as it overlaps with the $\Gamma_8(^4A_{2g}) \rightarrow \Gamma_8(^2T_{2g})$ transition. The intensity of the individual cooperative absorptions goes through a maximum corresponding to the transition to $\Gamma_8(^2E_g) + \Gamma_6(^2T_{1g})$ at 18 470 cm^{-1} (Figure 1). This behavior differs from that observed for K_2ReCl_6 and Cs_2ReCl_6, for which the intensity of the cooperative absorptions decreases rapidly as the transition energy increases, so that the transition to $\Gamma_6(^2T_{1g}) + \Gamma_6(^2T_{1g})$ could not be detected.[2] These differences in the intensity of the individual cooperative absorptions can be explained by the fact that the higher energy cooperative absorptions lie significantly closer to the lowest allowed LMCT transitions, from which intensity can be borrowed, in K_2TcCl_6 than in K_2ReCl_6 and Cs_2ReCl_6.[2,9,11,13]

The difference between the experimental energy of a cooperative absorption and the sum of the single ion transitions is defined as the exciton-exciton interaction energy.[14,15] These interaction energies range from 10 to 30 cm^{-1} for K_2ReCl_6, whereas their values are much more spread (from −65 to 288 cm^{-1}) for K_2TcCl_6, even allowing for the higher uncertainties of the experimental data for the latter compound. Due to the fact that the lattices of K_2ReCl_6 and K_2TcCl_6 are closely similar, as the two crystals are isostructural at room temperature with almost identical lattice parameters (±0.2%), this behavior cannot be ascribed to simple geometrical factors, but must involve differences in the coupling. The reasons for this behavior remain to be elucidated.

Acknowledgment. We thank Professor C. D. Flint (University of London) for many helpful and stimulating discussions and Professor R. Cappelletti (University of Parma) for the use of her optical equipment.

Registry No. K_2TcCl_6, 16923-46-9.

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Contribution from the Kuroda Solid Surface Project,
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Photochemical Grafting of Triosmium Dodecacarbonyl to Inorganic Metal Oxides

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Introduction

Metal carbonyl cluster compounds have attracted much attention as precursors for the preparation of highly dispersed supported metal catalysts.[1-4] A variety of transition-metal carbonyl clusters have been supported on metal oxides. Traditionally, metal clusters have been attached to supports by means of a thermally induced reaction between the metal carbonyl and surface hydroxyl groups.[5-16] However, thermal excitation often

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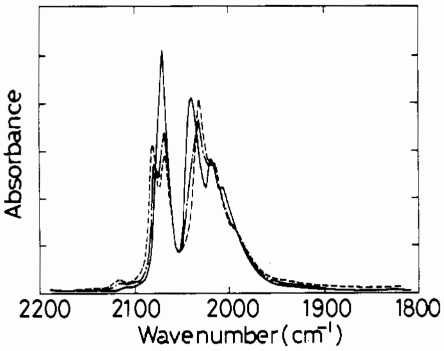

Figure 1. Light-induced FT-IR spectral changes of $Os_3(CO)_{12}$ physisorbed on SiO_2 versus time (min): (—) 0; (–·–) 10; (--) 20. Irradiation at 298 K by XeF excimer laser (351 nm, 5 Hz, 50 mJ/pulse).

results in undesired fragmentation of the metal framework rather than attachment of the intact metal cluster.[17,18] For example, triiron dodecacarbonyl cluster physisorbed on the surface of silica is known to undergo fragmentation when heated.[14-16]

We have recently shown that triiron dodecacarbonyl can be attached to the surface of silica via a photochemical route.[19] Selective photo-induced oxidative-addition reactions were also found to take place in the photolysis of $Ru_3(CO)_{12}$ supported on porous Vycor glass[20] or on Aerosil.[21] While the photochemistry of metal carbonyl clusters supported on solid surfaces has been little studied,[19-23] extensive investigations have been carried out on the photochemical processes of metal carbonyl clusters in solution.[24-35] In the solution state, the photochemical reaction of a metal carbonyl cluster is known to depend on the excitation wavelength and the temperature.[27,29,35] It is also known that metal carbonyl clusters with a metal skeleton composed of three or more metal atoms have a stronger tendency to undergo photoreaction of the ligands rather than metal–metal bond breaking in comparison with binuclear metal carbonyl clusters.[28-32]

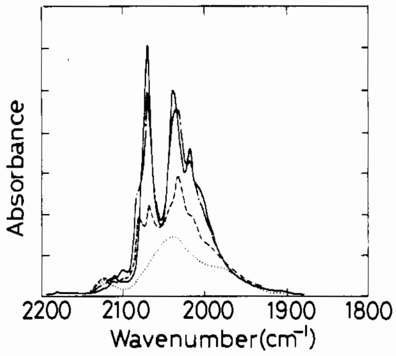

Figure 2. Light-induced FT-IR spectral changes of $Os_3(CO)_{12}$ physisorbed on SiO_2 versus time (min): (—) 0; (–·–) 3; (--) 50; (···) 190. Irradiation at 298 K by KrF excimer laser (248 nm, 5 Hz, 120 mJ/pulse).

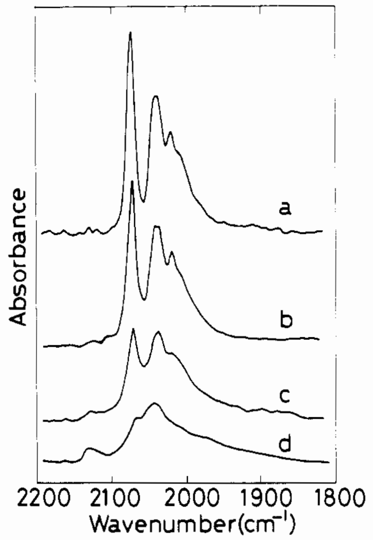

Figure 3. Light-induced FT-IR spectral changes of $Os_3(CO)_{12}$ physisorbed on SiO_2 versus time (min): (a) 0; (b) 10; (c) 20; (d) 30. Irradiation at 173 K by KrF excimer laser (248 nm, 5 Hz, 120 mJ/pulse).

In this paper, we report the results of our study on the photochemical grafting of triosmium dodecacarbonyl to the surface of silica and alumina.

Experimental Section

Triosmium dodecacarbonyl was obtained from Strem Chemical Co. and used without further purification. Silica aerogel (Aerosil 380), with a surface area of 380 m^2/g, was obtained from Nippon Aerosil. Alumina powder, with a surface area of 264 m^2/g, was obtained from CCI. Tetrahydrofuran (THF) (Nakarai GR Grade) was purified prior to use by distillation from $LiAlH_4$.

The support was dried for 12 h at 723 K under vacuum (1×10^{-4} Torr) prior to use. Under an oxygen- and water-free atmosphere in a

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drybox (Vacuum Atmospheres Co.), the support was impregnated with a 2×10^{-4} M THF solution of triosmium dodecacarbonyl so as to provide a nominal loading of 1 wt % osmium metal. The solvent was removed from the sample by trap-to-trap distillation on a glass vacuum line. The resulting powder was heated for 30 min between 373–423 K under vacuum (1×10^{-4} Torr) in order to effect complete dispersion of the carbonyl molecules on the support surface.

FT-IR spectra were obtained with a Nicolet 170SX FT-IR spectrometer. FT-IR spectra were measured in situ by using an evacuable reaction chamber equipped with two opposing quartz windows for light irradiation, which were oriented 90° relative to two KBr windows for FT-IR spectral measurements. The sample was held between two copper frames, which allowed it to be cooled or heated in the temperature range from 173 to 673 K. UV–visible diffuse-reflectance spectra were measured in the region of 200-900 nm by using a Shimadzu UV-265FS spectrometer equipped with an attachment for diffuse-reflectance measurements.

A deep-UV Xe lamp (Ushio UXM-501M 500 W) with a water filter to remove infrared radiation and a Toshiba C39A filter, which transmits light between 350 and 480 nm, was used for UV irradiation of the samples. An excimer laser (Lambda Physics 103 MSC) was used for irradiations at 248 nm (ArF gas) and 351 nm (XeF gas).

Results

Figure 1 shows the FT-IR spectrum of the triosmium dodecacarbonyl/silica system and its change at room temperature caused by XeF (351 nm) excimer laser excitation of the σ–σ^* band[36] of the carbonyl. The spectra clearly show the existence of isosbestic points. Clear isosbestic points were also exhibited in the UV–visible spectra (Figure 1S, supplementary material). The FT-IR spectra of the irradiated samples show bands at 2030 (s), 2065 (s), 2081 (s), and 2115 (w) cm^{-1}, which correspond to those known for the thermally produced hydridotriosmium dodecacarbonyl cluster attached to silica, $HOs_3(CO)_{10}$—OSi≡.[5,6,8] These spectra were obtained on a sample that was pretreated at 423 K for 30 min under vacuum to effect complete dispersion of the metal carbonyl on the support surface. Without this pretreatment, irradiation of the sample produced only a broad peak at 2000 cm^{-1} in the FT-IR spectrum. No clear peaks characteristic of the attached trinuclear or mononuclear osmium species were observed.

When the pretreated triosmium dodecacarbonyl/silica system was irradiated at room temperature by KrF excimer laser (248 nm) at the metal-to-ligand charge-transfer (MLCT) band,[36] its FT-IR spectrum exhibited the changes shown in Figure 2. The observed changes in the FT-IR spectrum indicate the formation of attached trinuclear and mononuclear osmium species. Further irradiation at 248 nm led to disappearance of the IR bands characteristic of the trinuclear species. Only the mononuclear osmium species,[18] with prominent absorptions at 2125 (w), 2040 (s, br) and 1975 (sh) cm^{-1}, was found to remain after prolonged irradiation. In contrast, when the same irradiation was made at 173 K, the mononuclear species was formed without any indication of formation of attached trinuclear species, as can be seen by the spectral changes shown in Figure 3.

We also investigated the effects of light irradiation on the attached triosmium dodecacarbonyl/silica system that was produced by the conventional thermal process.[5,6] In this case, irradiation by XeF excimer laser (351 nm) or Xe lamp (350-480 nm) at room temperature did not produce any significant changes in the FT-IR spectrum. At room temperature as well as at 173 K, irradiation by KrF excimer laser (248 nm) produced changes in the FT-IR spectrum indicative of transformation to the attached mononuclear species (Figure 2S, supplementary material).

In the case of the triosmium dodecacarbonyl/alumina system, excitation of the $\sigma^{*\prime}$–σ^* band of the carbonyl cluster produced prominent peaks in the FT-IR spectrum at 2045 (s) and 2130 (w) cm^{-1}. These two FT-IR peaks can be attributed to the surface-attached mononuclear osmium carbonyl species, $Os(CO)_3$—(O-Al≡)$_2$.[6] Interestingly, prolonged irradiation (350–480 nm) of the aluminum-attached triosmium cluster (prepared thermally) produced no change in the FT-IR spectrum.

Discussion

As mentioned above, we found that the photochemical behaviors were significantly different between the samples pretreated at 373–423 K and those without this pretreatment. This fact indicates that the photochemical process caused by irradiation depends significantly on the dispersion of the carbonyl molecules on the support surface. Following impregnation and solvent removal, the triosmium carbonyl cluster molecules are in an aggregated state. Photolysis of this material results in decomposition of the triosmium carbonyl cluster molecules. However, in the case of the highly dispersed system produced by thermal pretreatment, individual cluster molecules are in direct contact with surface hydroxyl groups. Irradiation of the dispersed cluster leads to facile reaction between the cluster and surface hydroxyl groups, with little interference from other deactivation processes.

The results obtained indicate that the photochemical reaction caused by σ–σ^* or $\sigma^{*\prime}$–σ^* band excitation of dispersed triosmium carbonyl cluster involves reaction with surface hydroxyl groups. The FT-IR and UV–visible spectra shown in Figures 1 and 1S (supplementary material), respectively, exhibit clear isosbestic points, which indicate that this reaction occurs with high selectivity.

In contrast to the triosmium dodecacarbonyl/silica system, σ–σ^* band excitation of the triosmium carbonyl cluster supported on alumina directly produces the attached mononuclear carbonyl. In the case where the trinuclear cluster was attached by thermal reaction to alumina and then irradiated in the region of 350–480 nm, no photochemical change took place. This shows that formation of the attached mononuclear by $\sigma^{*\prime}$–σ^* band excitation does not proceed via an attached trinuclear species.

The selectivity for these reactions is determined by the nature of the cluster and the reactivity of the surface hydroxyl group. This is much the same as the photochemistry of metal carbonyl clusters in solution where the reaction pathway is determined by the nature of the cluster and the type of ligands present.

The process resulting from excitation of the MLCT band of triosmium dodecacarbonyl on silica is more complicated than the process induced by σ–σ^* (or $\sigma^{*\prime}$–σ^*) band excitation. In addition to the oxidative-addition reaction leading to the attached trinuclear species, a fragmentation reaction forming attached mononuclear species also occurs. At 173 K, the process leading to the mononuclear species appears to be the sole process. The formation of the attached trinuclear cluster could be either a direct process from the MLCT excited state or an indirect process via the σ–σ^* or $\sigma^{*\prime}$–σ^* excited state, generated by internal conversion from the excited MLCT state. Formation of the attached mononuclear species may also occur either by a direct process from the MLCT state or by an indirect process via the attached trinuclear cluster, which is formed by one of the two processes mentioned above. The results of the present study do not allow us to discern between these alternative routes.

Conclusion

The photochemical grafting of triosmium dodecacarbonyl to silica and alumina was investigated. The photochemical behavior of triosmium dodecacarbonyl physisorbed on silica shows strong excitation wavelength dependence and high selectivity. Room-temperature excitation of the σ–σ^* (or $\sigma^{*\prime}$–σ^*) band leads to selective reaction between the cluster and surface hydroxyl groups to form the attached trinuclear species $HOs_3(CO)_{10}$—O—Si≡. In contrast, room-temperature irradiation of the MLCT band leads to formation of a mixture of the attached trinuclear cluster and the attached mononuclear carbonyl, whereas the same irradiation at 173 K results in selective formation of the attached mononuclear carbonyl. On alumina, room-temperature irradiation of the $\sigma^{*\prime}$–σ^* band results in selective formation of the attached mononuclear species. The selectivities of these reactions are determined by the inherent reactivity of the cluster and the nature of the surface hydroxyl groups.

Registry No. $Os_3(CO)_{12}$, 15696-40-9; SiO_2, 7631-86-9; Al_2O_3, 1344-28-1.

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Supplementary Material Available: Figure 1S (UV-visible spectral changes for UV irradiation (350-480 nm) of triosmium dodecacarbonyl physisorbed on silica) and Figure 2S (FT-IR spectral changes for KrF (248 nm) excimer irradiation of triosmium carbonyl hydride thermally attached to silica) (2 pages). Ordering information is given on any current masthead page.

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Dynamic Exchange between the Covalent and Dative Metal-Metal Bonded Isomers of the Heterodinuclear Complex $[NiPd(CNMe)_3(dppm)_2][PF_6]_2$ by $^{31}P\{^1H\}$ NOESY

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Received April 4, 1990

Nuclear Overhauser enhancement spectroscopy (NOESY) has been utilized extensively in studies of cross-relaxation and chemical-exchange processes.[1-8] To date, all reports of NOESY exchange studies have involved ^1H and ^{13}C nuclear magnetic resonance spectroscopy.[6-8] Here we describe the first quantitative dynamic study by $^{31}P\{^1H\}$ NOESY. The heterodinuclear complex $[NiPd(CNMe)_3(dppm)_2][PF_6]_2$ (**1**) and its preparation by transmetalation of $Ni_2(CNMe)_3(dppm)_2$ were reported previously.[9] We now describe our studies of the exchange between a pair of isomers of complex **1** that differ in their modes (covalent vs dative) of metal-metal bonding.

Experimental Section

Materials. All manipulations were performed under an atmosphere of dry N_2. Solvents were reagent grade and were distilled from the appropriate drying agents. All solvents were deoxygenated prior to use. The preparations of the complexes $[Ni_2Pd(CNMe)_6(dppm)_2][PF_6]_2$[9] and $[Ni_2Pt(CNMe)_5(dppm)_2][PF_6]_2$[10] are reported elsewhere.

Physical Measurements. Elemental analyses were performed by Galbraith Laboratories, Inc. Infrared spectra were recorded on a Perkin-Elmer 1710 FTIR instrument equipped with a Perkin-Elmer 3600 data station. ^1H NMR and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian XL-200 spectrophotometer. ^1H and $^{31}P\{^1H\}$ NMR chemical shifts were referenced to internal TMS and external 85% H_3PO_4 respectively.

Preparation of $[NiPd(CNMe)_3(dppm)_2][PF_6]_2$ (1). A solution of the starting material $[Ni_2Pd(CNMe)_6(dppm)_2][PF_6]_2$[9] in CH_2Cl_2 was stirred under N_2 until the $\nu(CN)$ bands characteristic of the starting material were replaced by new bands at 2226 (sh), 2202 (s), and 2152 (s) cm^{-1}. The resulting red solution was filtered to remove an insoluble yellow material, and the filtrate was concentrated under reduced pressure. Ether was added to facilitate precipitation, and the solution was cooled at −10 °C to obtain **1** as a red-purple solid in 80% yield. Anal. Calcd for $NiPdC_{56}H_{53}F_{12}N_3P_6$: C, 49.73; H, 3.94; N, 3.12. Found: C, 49.62; H, 4.21; N, 2.99. ^1H NMR (CD_2Cl_2): δ 7.3 (m, 40 H), 4.40 (s, 4 H), 2.71 (s, 6 H), 2.57 (s, 3 H). $^{31}P\{^1H\}$ NMR (CH_2Cl_2): δ 8.0 (t, P_A), 2.6 (t, P_B) (AA′BB′, $^2J(AB) + {}^4J(AB') = 124$ Hz). IR (KBr), $\nu(CN)$: 2220 (sh), 2184 (s), 2137 (s) cm^{-1}.

Preparation of $[NiPt(CNMe)_3(dppm)_2][PF_6]_2$ (2). The preparation of **2** was carried out by the same method as **1** but from the starting material $[Ni_2Pt(CNMe)_5(dppm)_2][PF_6]_2$.[10] Compound **2** was isolated as a dark orange solid, in 84% yield. Anal. Calcd for $NiPtC_{56}H_{53}F_{12}N_3P_6$: C, 46.85; H, 3.72; N, 2.93. Found: C, 46.17; H, 3.82; N, 2.39. ^1H NMR (CD_2Cl_2): δ 7.40 (m, 40 H), 4.55 (s, 4 H), 2.64 (s, 6 H), 2.30 (s, 3 H). $^{31}P\{^1H\}$ NMR (CH_2Cl_2): δ 12.62 (t, P_A), 9.25 (t, P_B) (AA′BB′, $^2J(AB) + {}^4J(AB') = 109.35$ Hz, $J(PtP_A) = 2455$ Hz). IR (KBr), $\nu(CN)$: 2232 (s), 2198 (s), 2145 (s) cm^{-1}. IR (CH_2Cl_2), $\nu(CN)$: 2228 (s), 2203 (s), 2146 (s) cm^{-1}.

Results and Discussion

The heterodinuclear complexes $[NiM(CNMe)_3(dppm)_2][PF_6]_2$ (M = Pd (**1**), Pt (**2**)) were prepared by elimination of $Ni(CNMe)_x$ (x = 2-3) from the heterotrinuclear clusters $[Ni_2Pd(CNMe)_6(dppm)_2][PF_6]_2$[9] and $[Ni_2Pt(CNMe)_5(dppm)_2][PF_6]_2$.[10] Complex

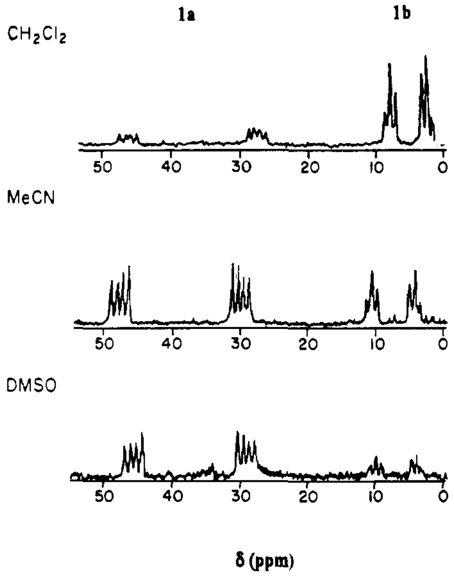

Figure 1. $^{31}P\{^1H\}$ spectra of the complex $[NiPd(CNMe)_3(dppm)_2][PF_6]_2$ (**1**) showing the different relative quantities of isomers **1a** and **1b** in the solvents CH_2Cl_2, MeCN, and DMSO.

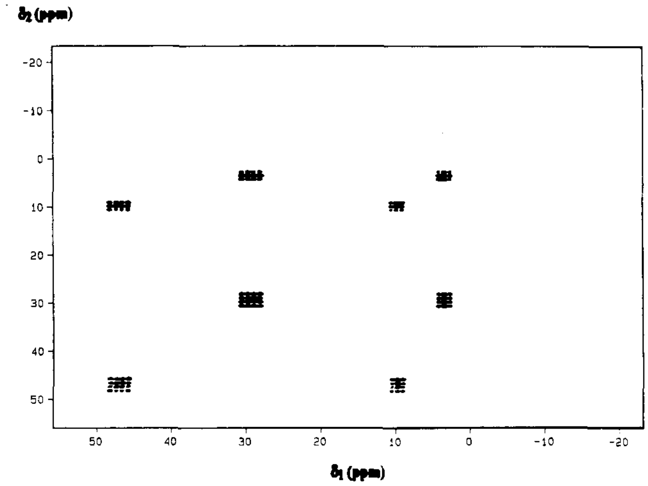

Figure 2. $^{31}P\{^1H\}$ 2D NOESY spectrum of the complex $[NiPd(CNMe)_3(dppm)_2][PF_6]_2$ (**1**) in MeCN. The features along the diagonal correspond to **1a** (lower left) and **1b** (upper right). Cross peaks show correlations between the high-field AA′BB′ multiplet components of **1a** and **1b** and similar correlations between the low-field multiplet components.

Table I. Equilibrium Constants and Free Energy Differences of Isomers **1a** and **1b** in CH_2Cl_2, CH_3CN, and DMSO, at 25 °C[a]

solvent	K_{ab}	$\Delta G°$, kJ/mol
CH_2Cl_2	3.5	-3.1
CH_3CN	0.85	0.41
DMSO	0.28	3.2

[a] K_{ab} = [**1b**]/[**1a**]; $\Delta G° = -RT \ln K_{ab}$

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