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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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 ν(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), ν(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), ν(CN): 2232 (s), 2198 (s), 2145 (s) cm^{-1}. IR (CH_2Cl_2), ν(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

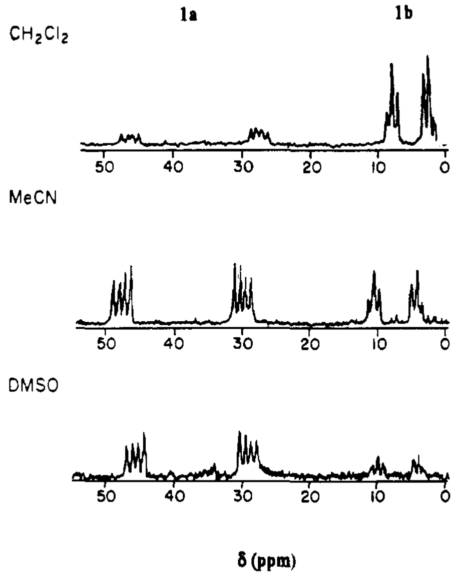

Figure 1. $^{31}P\{^1H\}$ spectra of the complex $[NiPd(CNMe)_3(dppm)_2][PF_6]_2$ (**1**) showing the different relative quantities of isomers **1a** and **1b** in the solvents CH_2Cl_2, MeCN, and DMSO.

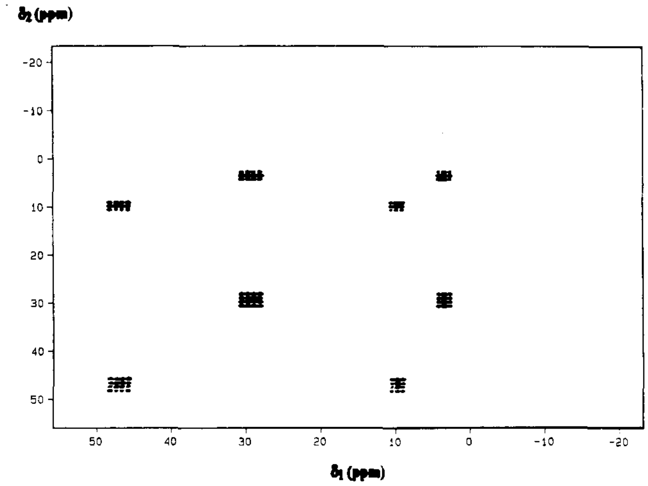

Figure 2. $^{31}P\{^1H\}$ 2D NOESY spectrum of the complex $[NiPd(CNMe)_3(dppm)_2][PF_6]_2$ (**1**) in MeCN. The features along the diagonal correspond to **1a** (lower left) and **1b** (upper right). Cross peaks show correlations between the high-field AA'BB' multiplet components of **1a** and **1b** 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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1 exists in solution as two conformatinal isomers, **1a** and **1b**. The exchange rate between **1a** and **1b** is so slow that each isomer can be observed independently by $^{31}P\{^1H\}$ NMR spectroscopy up to 80 °C. The $^{31}P\{^1H\}$ NMR spectra recorded in different solvents show a dependence of the relative populations of isomers **1a** and **1b** on solvent polarity (Figure 1).

The ^{31}P T_1 values of isomers **1a** and **1b** are identical (4.5 s); thus, the integrated intensities of the individual AA′BB′ multiplets for **1a** and **1b** allow the evaluation of the equilibrium constants $K_{ab} = [\mathbf{1b}]/[\mathbf{1a}]$. The equilibrium constants and the corresponding free energy differences are summarized in Table I. Isomer **1a** is thermodynamically less stable than **1b** in the least polar solvent CH_2Cl_2, comparably stable in CH_3CN, and much more stable in the most polar solvent DMSO. The exchange process between **1a** and **1b** has been unambiguously established by a $^{31}P\{^1H\}$ NOESY experiment (Figure 2).

In contrast to the pair of isomers observed for **1**, the heterodinuclear platinum complex **2** exists in solution as a single species, irrespective of solvent. The $^{31}P\{^1H\}$ NMR, FTIR, and ^1H NMR spectra of **2** are very similar to those of isomer **1b**. However, the observable platinum–phosphorus coupling in complex **2** enables us to distinguish the dppm phosphorus atoms coordinated to platinum from those coordinated to nickel. The downfield half of the AA′BB′ spectrum of complex **2** displays platinum–phosphorus coupling. By analogy, we assign the downfield half of the AA′BB′ spectrum of **1b** to the phosphorus atoms connected to palladium. From the $^{31}P\{^1H\}$ NOESY spectrum of **1a** and **1b**, it can be determined that the downfield half of the AA′BB′ spectrum of **1a** also corresponds to the phosphorus atoms connected to palladium. The downfield features of the spectra of **1a** and **1b** are clearly correlated.

NOESY is an excellent alternative for studying exchange processes quantitatively, inasmuch as we were unable to observe direct coalescence between **1a** and **1b** up to 80 °C. The $^{31}P\{^1H\}$ NOESY spectrum of **1** in CH_3CN at 25 °C is well suited for quantitative analysis since the cross peaks and diagonal peaks are distinct and the J cross peaks, which appear at short mixing times, τ_m, do not interfere with the conformational exchange cross peaks. The fact that all of the phosphorus atoms of **1a** and **1b** have the same T_1 (4.5 s) in MeCN allows the reliable use of the integrated intensities of peaks in the $^{31}P\{^1H\}$ NOESY for the evaluation of exchange rate constants. The phosphorus atoms coordinated to Pd exhibit the same exchange rate as those coordinated to Ni, for both **1a** and **1b**. The exchange rate constants of the phosphorus atoms coordinated to Pd are therefore representative of the whole molecule. The exchange process between **1a** and **1b** may thus be simplified to an unequally populated one-spin/two-site system. The equations for evaluation of exchange rate constants in an unequally populated one-spin/two-site system are derived from Ernst's general equations for the mixing coefficients a_{ij} of cross and diagonal peaks (eq 1–4).[2]

$$K\tau_m = \ln \frac{\chi_b + (a_{ab}/a_{aa})\chi_b}{\chi_b - (a_{ab}/a_{aa})\chi_a} \tag{1}$$

$$K\tau_m = \ln \frac{\chi_a + (a_{ab}/a_{bb})\chi_a}{\chi_a - (a_{ab}/a_{bb})\chi_b} \tag{2}$$

$$K = k_{ab}/\chi_b = k_{ba}/\chi_a \tag{3}$$

$$\chi_a + \chi_b = 1 \tag{4}$$

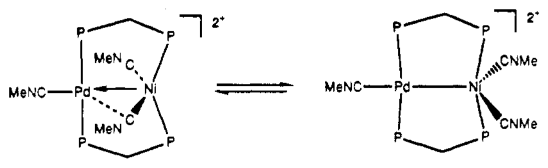
In general, ^1H NOESY studies reveal that the reliability of the cross peak intensities depends on mixing time and molecular weight.[3] Thus a single 2D spectrum at fixed τ_m cannot produce reliable quantitative dynamic results; variation of the mixing time is necessary. The $^{31}P\{^1H\}$ NOESY of **1** in CH_3CN has been studied over the range of mixing times 0.1, 0.05, 0.01, and 0.005 s (Table II). Ideally the k_{ab} and k_{ba} values calculated from eq 1 should be identical with those calculated from eq 2 for the same fixed τ_m. The statement holds true for mixing times $\tau_m = 0.01$ and 0.005 s. For the mixing times of 0.1 and 0.05 s, the exchange rate constants obtained from eq 1 deviate significantly from the resultls obtained by eq 2. This implies that the results obtained at longer mixing times are of limited validity. We suggest that the exchange rate constants obtained for the shorter mixing times of 0.01 and 0.005 s are reliable. The equilibrium constant derived from $k_{ab}/k_{ba} \simeq 0.88$ at $\tau_m = 0.01$ s is essentially identical with the value acquired from the 1D $^{31}P\{^1H\}$ NMR integration of **1a** and **1b** in acetonitrile. Therefore, the exchange rate constants for **1a** and **1b** are $k_{ab} = 9.21$ s^{-1} and $k_{ba} = 10.5$ s^{-1}, respectively. The free energies of activation, $\Delta G^{\ddagger}_{ab}$ and $\Delta G^{\ddagger}_{ba}$, for the exchange process between **1a** and **1b** in CH_3CN are 67.5 and 67.2 kJ/mol, respectively.

Table II. Exchange Rate Constants and Equilibrium Constants of Isomers **1a** and **1b** in CH_3CN at 25 °C[a]

τ_m, s	eq	k_{ab}, s^{-1}	k_{ba}, s^{-1}	K_{ab}
0.1	1	12.4	17.9	0.693
	2	6.85	9.86	0.695
0.05	1	10.5	14.1	0.745
	2	8.80	11.8	0.746
0.01	1	9.21	10.5	0.877
	2	9.06	10.3	0.880
0.005	1	8.28	8.86	0.935
	2	8.26	8.85	0.933

[a] $K_{ab} = k_{ab}/k_{ba}$.

The observed exchange process is assigned to the interconversion between the dative (**1a**) and covalent (**1b**) metal-metal bonded isomers of **1** (eq 5). In the solid state, complex **1** exhibits a "mixed geometry" structure with locally tetrahedral Ni and rectilinear Pd coordination geometries.[9] The solid-state structure is consistent with a Ni(0)/Pd(II) formulation and hence a dative Ni(0)→Pd(II) interaction. The IR spectrum of **1** in DMSO, where **1a** is the predominant species, closely resembles the IR spectrum of crystalline **1** in a KBR pellet. We thus attribute a dative Ni–Pd-bonded structure to **1a**. We have been completely unsuccessful at growing crystals of isomer **1b** or the platinum complex **2**. However, the preferential stabilization of **1a** in polar solvents, indicated by the $^{31}P\{^1H\}$ NMR data (Figure 1), suggests that 1a is a significantly more polar species than **1b**. The significant polarity difference between **1a** and **1b** is consistent with the general observation, reported by Pomeroy and co-workers,[12] that complexes containing dative metal–metal bonds are more polar than those containing covalent metal–metal bonds. We suggest that isomer **1b** possesses a less polar, covalent σ-Ni(I)–Pd(I) interaction. This suggestion is supported by electronic absorption spectroscopic data. Solutions of **1** in polar solvents such as DMSO and MeCN are deep purple due to an intense electronic transition at 565 nm. This band is much less intense in less polar solvents such as CH_2Cl_2; and no additional bands emerge over the $\lambda > 300$ nm region of the spectrum. These results suggest that the less polar isomer **1b** undergoes no allowed electronic transitions in the visible region. All electronic transitions of significant intensity for **1b** occur at $\lambda < 300$ nm. The relatively uncomplicated, high-energy absorption spectrum of **1b** is similar to the σ,σ^* spectra of covalently σ-bonded binuclear palladium complexes.[13] The exchange process observed



(5)

1a **1b**

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by $^{31}P\{^1H\}$ NOESY is ascribed to the relatively slow interconversion between the covalent and dative Ni–Pd-bonded isomers of **1**.

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IR Evidence for the Formation of an η^2(C,O)-α-Ketoacyl Complex upon Low-Temperature Photolysis of (η-C_5H_4Me)(CO)(NO)Mn–C{O}C{O}Tol

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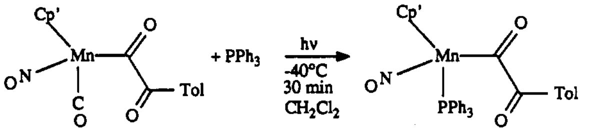
A surprising feature of the chemistry of the α-ketoacyl complex Cp′(CO)(NO)Mn-C{O}C{O}Tol (**1**) (Cp′ = η-C_5H_4Me) is its resistance to CO deinsertion to form an acyl complex when either heated or irradiated.[1] Photolysis of **1**, for example, in the presence of PPh_3 did not lead to deinsertion but instead gave clean photosubstitution of PPh_3 (eq 1).[1] It was thought that this result might be due to the formation of an intermediate with an α-ketoacyl ligand coordinated in an η^2(C,O) fashion that stabilizes the coordinatively unsaturated complex resulting from photoinduced CO loss. To address this question, a detailed low-temperature photochemical study of **1** was undertaken, and those results are reported herein.



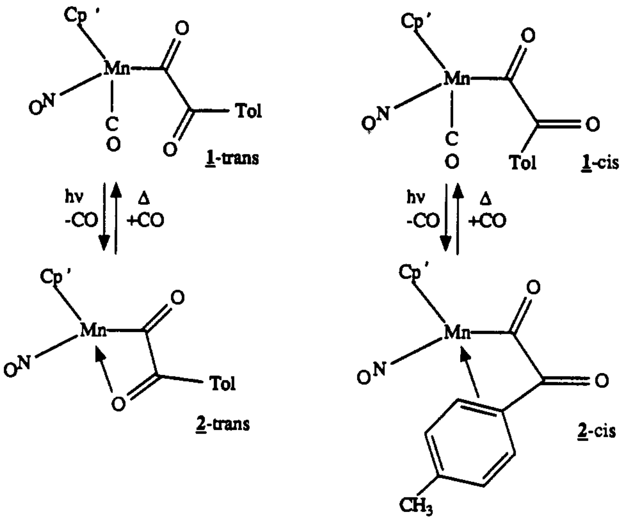
(1)

Experimental Section

Complex **1** was prepared as described in ref 1. Solvents used were dried by distillation from $CaCl_2$ (CH_2Cl_2) or Na (2-MeTHF). IR spectra were recorded on a Nicolet 7199B FTIR spectrometer using a liquid-nitrogen-cooled MCT detector (32 scans, resolution 1.0 cm^{-1}). For the low-temperature measurements, use was made of an Oxford Instruments DN 1704/54 liquid-nitrogen cryostat. All photochemical experiments were conducted by using the 436-nm line of an Osram HBO 200W/2 200-W Hg lamp.

Results

Scheme I



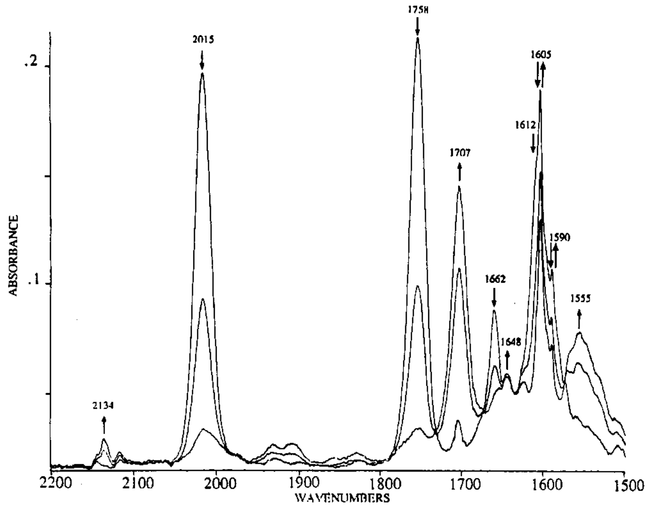


Figure 1. IR spectral changes occurring upon 436-nm irradiation of complex **1** in CH_2Cl_2 at −100 °C.

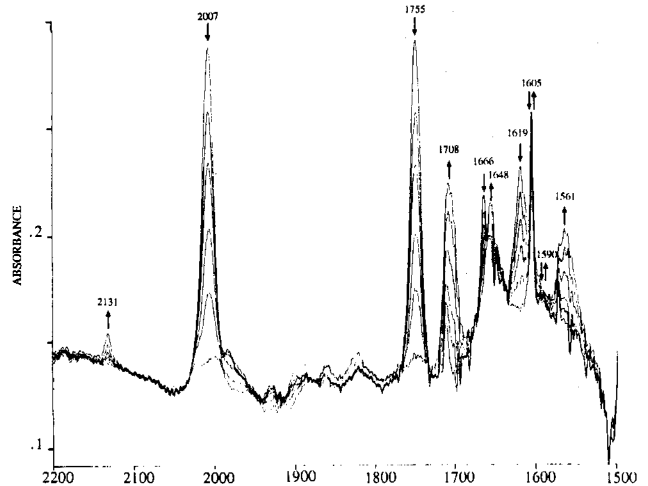


Figure 2. IR spectral changes occurring upon 436-nm irradiation of complex **1** in 2-MeTHF at −140 °C.

Complex **1** was studied at −140 °C in 2-MeTHF and at −100 °C in CH_2Cl_2, conditions under which both s-cis (**1**-cis) and s-trans (**1**-trans) isomers of the α-ketoacyl ligand are present (see Scheme I). Table I lists the IR bands observed for these isomers and their assignments. Like the previously studied palladium α-ketoacyl

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