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Scrambling of Halide Ligands between Palladium(II) and between Palladium(I) Complexes of Bis(diphenylphosphino)methane. Observation of Unusual Temperature-Dependent Phosphorus-31 Nuclear Magnetic Resonance Chemical Shifts

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Halogen-exchange equilibria between bis(diphenylphosphino)methane (dpm) complexes of palladium(II), $Pd(dpm)X_2$ (X = halide), and between complexes of palladium(I), $Pd_2(dpm)_2X_2$, have been examined by ^{31}P NMR spectroscopy. Equilibria in noncoordinating, nonpolar solvents such as dichloromethane are established within 5 min and result in nearly statistical distributions of halide ligands. Mixed-halide complexes of the type $Pd_2(dpm)_2XY$ show temperature-dependent ^{31}P NMR spectra that are analyzed in terms of temperature-dependent chemical shifts for the two types of phosphorus atoms. For $Pd_2(dpm)_2ClI$, the two chemical shifts approach each other, are identical at 35 °C, and then move apart at higher temperature.

Introduction

During our extensive studies[1-11] of the reaction and structural chemistry of palladium complexes of bis(diphenylphosphino)methane (dpm), we have had occasion to examine reactions in which the scrambling of halide ligands occurs. Two reactions have been examined in detail. One involves the exchange of halide ligands between palladium(II) monomers as shown in eq 1 (X = Cl, Br, I). The other involves an

$$Pd(dpm)X_2 + Pd(dpm)Y_2 \rightleftharpoons 2Pd(dpm)XY \qquad (1)$$

analogous process for dimeric complexes of palladium(I) and is represented by eq 2.

$$Pd_2(dpm)_2X_2 + Pd_2(dpm)_2Y_2 \rightleftharpoons 2Pd_2(dpm)_2XY \qquad (2)$$

Two features of these reactions are noteworthy. In both cases equilibria between the three complexes are rapidly established in relatively nonpolar and noncoordinating solvents. These equilibria are readily followed by observing the ^{31}P NMR spectra of the components. The ^{31}P NMR spectra of the mixed-halide complexes $Pd_2(dpm)_2XY$, but not Pd(dpm)XY, show remarkable changes at different temperatures that are due to unusual temperature dependences of the ^{31}P chemical shifts.

Experimental Section

Preparation of Compounds. $Pd_2(dpm)_2X_2$[3] and $Pd(dpm)X_2$[12] were prepared by established routes.

Physical Measurements. ^1H (5-mm tubes, 200 MHz) and $^{31}P\{^1H\}$ (12-mm tubes, 81 MHz) were recorded on a Nicolet NT-200 Fourier transform spectrometer. Temperature control was maintained for all spectral runs. An external 85% phosphoric acid reference was used for ^{31}P NMR spectra, and the high-frequency-positive convention recommended by IUPAC is used in reporting chemical shifts. T_1 measurements indicated that all phosphorus atoms in the complexes examined here had comparable relaxation rates so that integrations of resonance amplitudes give valid relative ratios of the amounts of individual species. Spectral analysis was carried out with a noniterative simulation routine available with the Nicolet software.

Table I. NMR Parameters and Formation Constants for Palladium(II) Complexes

	^1H NMR $(PCH_2P)^a$		^{31}P NMR^b			
compd	δ	J(P–H), Hz	δ	δ	J(P–P), Hz	$K_f^{b,c}$
Pd(dpm)ClBr	4.30	10.2 (t)	−53.1	−56.4	63.7	3.3 ± 0.3
Pd(dpm)BrI	4.42	10.4 (t)	−54.1	−64.2	57.3	3.1 ± 0.1
Pd(dpm)ClI	4.39	10.6 (t)	−52.8	−63.8	60.7	2.1 ± 0.3
$Pd(dpm)Cl_2$	4.28	10.8 (t)	−53.7			
$Pd(dpm)Br_2$	4.33	10.6 (t)	−55.7			
$Pd(dpm)I_2$	4.55	10.4 (t)	−62.7			

[a] In CD_2Cl_2 solution at 24 °C. [b] In $CDCl_3$ solution at 24 °C. [c] Equilibrium constants for the reaction $Pd(dpm)X_2$ + Pd(dpm)Y $Pd(dpm)Y_2 \rightleftharpoons 2Pd(dpm)XY$ in $CDCl_3$ at 24 °C.

Results

Halogen Exchange between Palladium(II) Complexes. The halogen-exchange reaction (1) is readily monitored by either ^{31}P or ^1H NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum of a mixture of $Pd(dpm)X_2$ and $Pd(dpm)Y_2$ consists of two singlets due to the initial components and an AB quartet, which is readily assigned to the mixed-halide species Pd(dpm)XY. The latter has two inequivalent phosphorus atoms. The appropriate NMR parameters are set out in Table I. The P–P coupling constants are consistent with the presence of cis phosphorus atoms in the mixed-halide complexes.[13] The chemical shifts of the two dissimilar phosphorus atoms in Pd(dpm)XY lie to slightly higher and slightly lower frequency than the resonance of the $Pd(dpm)X_2$ and $Pd(dpm)Y_2$.

The formation of the mixed-halide species may also be followed by ^1H NMR spectroscopy. The methylene protons of the dpm ligand are unusually good structural probes. In the present case triplets due to P–H coupling are expected with ^2J(P–H) of ca. 10 Hz.[8] Indeed separate resonances (triplets) are readily detected for each of the three components of eq 1 in the 200-MHz ^1H NMR spectra. The relevant spectral parameters are set out in Table I.

At 24 °C the equilibria expressed in eq 1 are established within 5 min, the time necessary for us to prepare solutions and obtain their ^{31}P NMR spectra. No intensity changes occur in the spectra when they are monitored for several hours after mixing. Because of the rapidity with which these equilibria are established, no attempts have been made to isolate the mixed-halide species. Integration of the ^{31}P NMR spectra allows calculation of the equilibrium constants for reaction

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Table II. $^{31}P\{^1H\}$ and ^1H NMR Data for Palladium(I) Complexes

	$^{31}P\{^1H\}^a$			$^1H(CH_2)^b$	
compd	δ_{P_A}	δ_{P_B}	J(PP), Hz	δ	J(PH),[c] Hz
$Pd_2(dpm)_2Cl_2$	−2.5			4.17 (q)	4.0
$Pd_2(dpm)_2Br_2$	−4.7			4.22 (q)	4.0
$Pd_2(dpm)_2I_2$	−10.3			4.27 (q)	4.0
$Pd_2(dpm)_2ClBr$[f]	−3.0	−4.3	43.2, 35.5[d]	*e*	
$Pd_2(dpm)_2BrI$[f]	−7.23	−7.95	39[g]	*e*	
$Pd_2(dpm)_2ClI$[f]	−6.4	−6.6	39[h]	*e*	

[a] Run in $CDCl_3$ at 24 °C, unless otherwise noted. [b] Run in CD_2Cl_2 at 24 °C, unless otherwise noted; q = quintet. [c] Apparent P–H coupling in a virtually coupled system. Analysis as a $X_2A_2A'_2$ (X = H, A = P) system indicates that the apparent J(PH) is actually the average of J(HP) and J(HP′) with J(PP′) larger than 100 Hz. [d] J(AB) and J(AB′) for an AA′BB′ spectrum. [e] Resonances due to the three equilibrated complexes overlap too severly for resolution. [f] These are not isolable complexes but only exist in solution in equilibrium with the symmetric parent dimers. [g] J(AB) for an A_2B_2 spectrum. [h] Run at −20 °C to effect signal resolution.

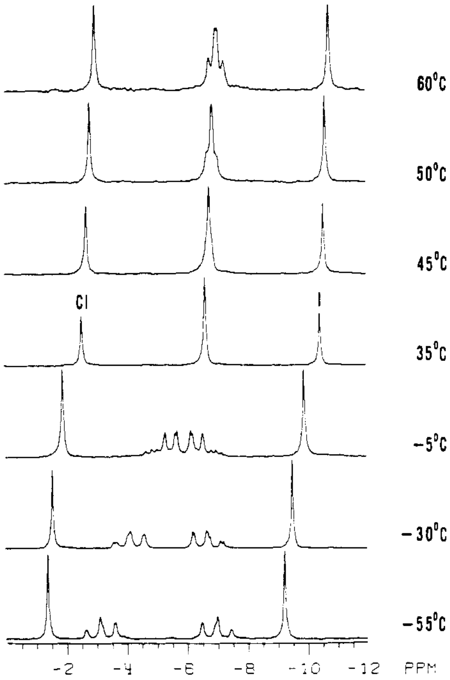

Figure 1. $^{31}P\{^1H\}$ NMR spectrum of a mixture of $Pd_2(dpm)_2Cl_2$ (Cl), $Pd_2(dpm)_2I_2$ (I), and $Pd_2(dpm)_2ClI$ (A_2B_2 pattern) as a function of temperature in chloroform solution.

1. These values are presented in the last column of Table I. Varing the mole ratio of reactants has no effect on the equilibrium constant calculated. Note that the values obtained are close to the value of 4 which is predicted on a simple statistical basis.

Halogen Exchange between Palladium(I) Complexes. The halogen exchange between dimeric palladium(I) complexes shown in eq 2 has been monitored by ^{31}P NMR spectroscopy. The ^1H NMR spectra of the methylene protons of the dpm ligands diplay overlapping resonances that are not convenient probes for the reactions. Relevant NMR data are given in Table II.

The ^{31}P NMR spectra of a mixture of $Pd_2(dpm)_2Cl_2$ and $Pd_2(dpm)_2I_2$ at various temperatures in chloroform-*d* solution are shown in Figure 1. The single resonances at ca. −2 and −10 ppm are due to $Pd_2(dpm)_2Cl_2$ and $Pd_2(dpm)_2I_2$, respectively. The chemical shifts and line widths of these resonances are identical with those of the individual species measured from isolated samples. The mixed-halide complex, $Pd_2(dpm)_2ClI$, is responsible for the additional resonances, which are readily analyzed as an A_2B_2 spin system.[14] Note that with increasing temperature the pattern of resonances due to $Pd_2(dpm)_2ClI$ becomes progressively compressed until at 35 °C only a single resonance is seen. Surprisingly, at higher temperatures the A_2B_2 pattern reemerges. These changes *cannot* be ascribed to a dynamic process which averages phosphorus environments. The usual line broadening, which would accompny such a process, does not occur. Neither the resonances of the parent complexes $Pd_2(dpm)_2Cl_2$ and $Pd_2(dpm)_2I_2$ nor those of the mixed-halide species, $Pd_2(dpm)_2ClI$, show any sign of significant increases in their line widths. Rather what is occurring

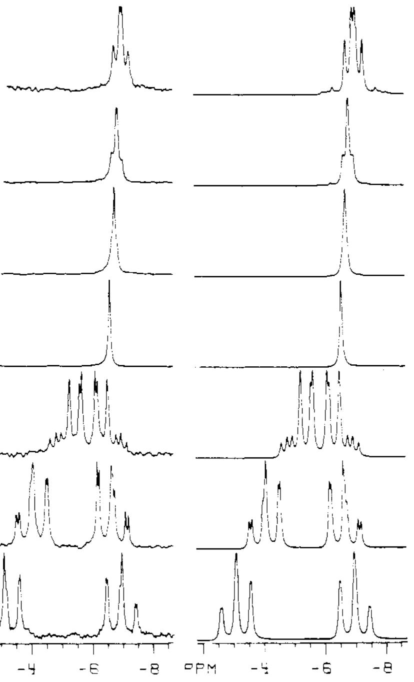

Figure 2. Temperature-dependent A_2B_2 $^{31}P\{^1H\}$ NMR spectra of $Pd_2(dpm)_2ClI$: left side, experimental spectra; right side, simulated spectra. The simulations maintain J_{AB} = 39 Hz throughout but vary the chemical shifts of the two phosphorus atoms. The temperatures for the experimental spectra are the same as shown in Figure 1.

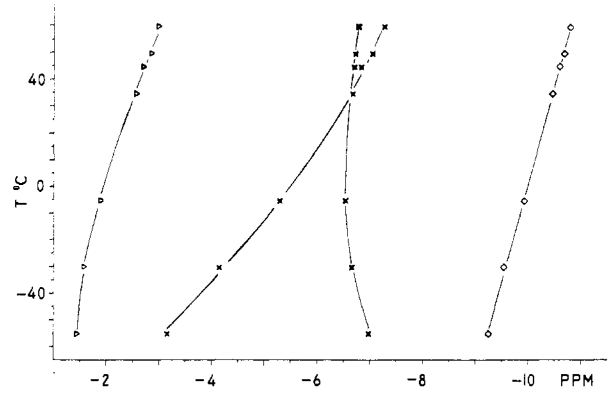

Figure 3. Plot of the temperature dependence of the chemical shits of $Pd_2(dpm)_2Cl_2$ (triangles), $Pd_2(dpm)_2I_2$ (diamonds), and $Pd_2(dpm)_2ClI$ (crosses) in chloroform solution.

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[14] The phosphorus NMR spectrum of $Pd_2(dpm)_2XY$ should belong to the AA′BB′ spin system. However, when J(AB) and J(AB′) approach each other in value, a simpler A_2B_2 spectrum may result. The ^{31}P NMR spectrum of $Pd_2(dpm)_2ClBr$, which displays an AA′BB′ pattern, does have similar values for J(A,B) and J(A,B′) and so it is not unreasonable to find that the values of J(A,B) and J(A,B′) in $Pd_2(dpm)_2ClI$ are accidentally the same. From these spectra it is not possible to obtain accurate values of J(A,A′) and J(B,B′). For spectral simulations values in the range 250–500 Hz were used.

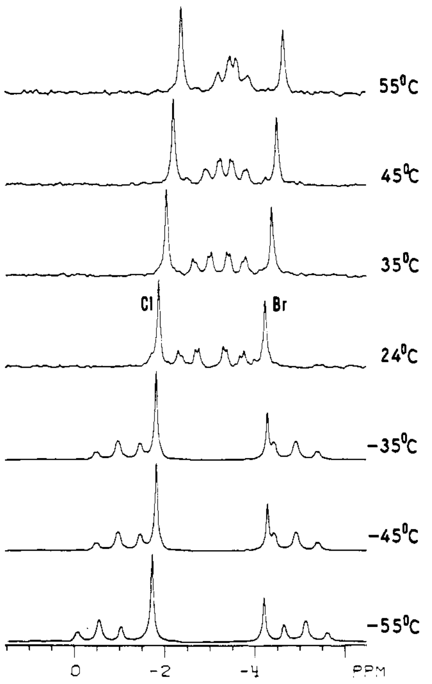

Figure 4. $^{31}P\{^1H\}$ NMR spectrum of a mixture of $Pd_2(dpm)_2Cl_2$ (Cl), $Pd_2(dpm)_2Br_2$ (Br), and $Pd_2(dpm)_2ClBr$ (A_2B_2 pattern) as a function of temperature in chloroform solution.

is a change in the ^{31}P chemical shifts of $Pd_2(dpm)_2ClI$. The effect is striking because, instead of a gradual drift of both chemical shifts in one direction, the two chemical shifts approach and apparently cross at 35 °C. All of the spectra are readily analyzed and simulated in terms of an A_2B_2 spin system with a single coupling constant, $J(AB) = 39$ Hz, and two variable chemical shifts. Although this system has been throughly analyzed in a standard text,[15] we have nevertheless presented a simulation of these spectra in Figure 2. The temperature dependence of the chemical shifts of the components are shown graphically in Figure 3.

The ^{31}P NMR spectra of a mixture of $Pd_2(dpm)_2Cl_2$ and $Pd_2(dpm)_2Br_2$ as a function of temperature are shown in Figure 4. The changes observed are again interpreted in terms of a pair of temperature-dependent chemical shifts for the two phosphorus atoms in the mixed-ligand species. In this case the speectra were analyzed in the AA′BB′ spin system with constant values of 43.2 and 35.7 Hz for $J(AB)$ and $J(AB')$. The temperature dependence of the chemical shifts are plotted in Figure 5. For this system, the crossing of the two chemical shifts is not observed within the accessible temperature range. However, at low temperatures the chemical-shift difference between the two phosphorus atoms in $Pd_2(dpm)_2ClBr$ exceeds the chemical-shift difference between $Pd_2(dpm)_2Cl_2$ and $Pd_2(dpm)_2Br_2$. The ^{31}P NMR spectra of a mixture of $Pd_2(dpm)_2Br_2$ and $Pd_2(dpm)_2I_2$ show only a modest temperature dependence.

The magnitude of the temperature dependence of the chemical shifts of $Pd_2(dpm)_2ClI$ varies with solvent. The largest effect is seen in chloroform. While qualitatively similar spectral changes are seen in other solvents including dichloromethane, dibromomethane, and 1,2-dichloroethane, the change in chemical-shift difference between the two phosphorus atoms is less than 1.5 Hz/deg whereas in chloroform it is about 3 Hz/deg.

We suspect that the temperature dependences of the ^{31}P NMR chemical shifts are a result of specific solvation, which is accentuated as the polar nature of the $Pd_2(dpm)_2XY$ is increased. The magnitude of the effect is clearly solvent dependent, and it also decreases as the electronegativity difference between the constituent halide ligands decreases. The size of the change in ^{31}P chemical shifts with temperature is not greatly different from that observed for other phosphorus compounds. For example, Dickert and Hellmann[16] have reported that the chemical-shift difference between the phosphorus atoms in triphenylphosphine and triphenylphosphine oxide (each 0.1 M in toluene-d_8 solution) increases by 1.3 Hz/deg over the temperature range −90 to +70 °C. For the symmetrical dimers such as $Pd_2(dpm)_2I_2$, the phosphorus chemical shift is decreasing by about 1.1 Hz/deg with increasing temperature over the temperature range −55 to +55°. The striking effect seen in the spectra of the unsymmetrical palladium complexes results from the fact that the two different phosphorus resonances in $Pd_2(dpm)_2XY$ are drifting toward one another rather than both gradually shifting in one direction. The effect seen in chloroform solution results in about a 3 Hz/deg decrease in the chemical-shift difference between the two phosphorus atoms in $Pd_2(dpm)_2XY$ upon warming. Clearly these observations offer a note of caution in regard to analysis of ^{31}P NMR spectra. Accidental chemical-shift similarities render the ^{31}P NMR spectrum of $Pd_2(dpm)_2ClI$ deceptively simple at 35 °C. In this case it is necessary to observe the effect of temperature on the spectrum in order to throughly analyze the spectrum.

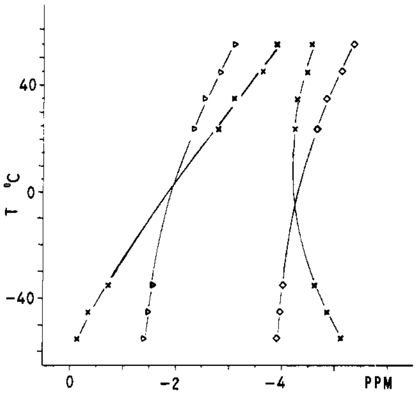

Figure 5. Plot of the temperature dependence of the chemical shifts of $Pd_2(dpm)_2Cl_2$ (triangles), $Pd_2(dpm)_2Br_2$ (diamonds), and $Pd_2(dpm)_2ClBr$ (crosses) in chloroform solution.

Table III. Equilibrium Data for Halide Ligand Scrambling between Palladium(I) Dimers

compd	solvent	K_{f_2}[a]	ΔH, kcal/mol	ΔS, cal/(mol deg)
$Pd_2(dpm)_2ClI$	CH_2Cl_2	6.4 ± 0.3	−1.2 ± 0.5	3.0 ± 1
	CH_2Br_2	6.9 ± 0.3	−1.0	2.8
	CH_2ClCH_2Cl	6.0 ± 0.3	−0.6	3.1
$Pd_2(dpm)_2ClBr$	$CHCl_3$	4.1 ± 0.3		
$Pd_2(dpm)_2BrI$	$CHCl_3$	4.3 ± 0.3		

[a] Equilibrium constant for the reaction 2 at 24 °C.

The ^{31}P NMR spectra can also be analyzed to give equilibrium constants for reaction 2. As is the case for the palladium(II) complexes, scrambling of halide ligands between palladium(I) complexes reaches equilibrium within the time necessary for sample preparation and observation. The values of K_f for formation of $Pd_2(dpm)_2XY$ by reaction 2 are recorded in Table III. In cases where appreciable variation of K_f as a function of temperature occurred, the values of ΔH and ΔS for this reaction were obtained. In chloroform solution there is little variation of K_f with temperature and the values of K_f

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are close to the statistically predicted value of 4.

Since these halide ligand scrambling reactions all occur in nonpolar, noncoordinating solvents and equilibria are rapidly established, we presume that the halogen interchange is occurring by the formation of halogen bridges between individual palladium complexes. Related observations of halide ligand scrambling of Pt(IV) phosphine complexes appears to involve catalysis by Pt(II).[17] For the 16-electron complexes described here, there is not electronic need to involve a redox step in the ligand exchange.

Acknowledgment. We thank the National Science Foundation (Grant CHE 7924515) for support and Matthey Bishop for a loan of palladium chloride.

Registry No. Pd(dpm)ClBr, 80594-57-6; Pd(dpm)BrI, 80594-58-7; Pd(dpm)ClI, 80594-59-8; Pd(dpm)Cl_2, 38425-01-3; Pd(dpm)Br_2, 77462-41-0; Pd(dpm)I_2, 77462-40-9; $Pd_2(dpm)_2Cl_2$, 64345-29-5; $Pd_2(dpm)_2Br_2$, 60482-68-0; $Pd_2(dpm)_2I_2$, 67477-87-6; $Pd_2(dpm)_2$ClBr, 80594-60-1; $Pd_2(dpm)_2$BrI, 80594-61-2; $Pd_2(dpm)_2$ClI, 80594-62-3.

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Axially Coordinated Tetrakis[*N*-(2,6-dimethylphenyl)acetamido]dimolybdenum(II) Compounds. Structures of $Mo_2[(xylyl)NC(CH_3)O]_4\cdot 2THF$ and $Mo_2[(xylyl)NC(CH_3)O]_4\cdot L$ ($L = NC_5H_5, NC_5H_4CH_3$)

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The structures of three axially coordinated tetrakis(xylylacetamido)dimolybdenum(II) compounds are reported (xylyl = 2,6-dimethylphenyl): $Mo_2[(xylyl)NC(CH_3)O]_4\cdot 2THF$ (**1**) and $Mo_2[(xylyl)NC(CH_3)O]_4\cdot L$ ($L = NC_5H_5$ (**2**), $NC_5H_4CH_3$ (**3**)). Compound **1** was solved in the orthorhombic space group *Pnna* with unit cell parameters $a = 20.147$ (5) Å, $b = 48.02$ (1) Å, $c = 16.485$ (4) Å, $V = 15949$ (11) $Å^3$, and $Z = 12$. Compound **2** crystallizes in the orthorhombic space group *Pccn* with unit cell parameters $a = 30.414$ (6) Å, $b = 17.371$ (3) Å, $c = 18.489$ (2) Å, $V = 9768$ (4) $Å^3$, and $Z = 8$. Compound **3** was solved in the orthorhombic space group *Pbcn* with cell parameters $a = 15.635$ (1) Å, $b = 18.272$ (1) Å, $c = 15.509$ (2) Å, $V = 4431$ (1) $Å^3$, and $Z = 4$. The crystals of **1** contain molecules on general positions and also on special positions where a twofold axis is collinear with the Mo–Mo bond. The two sorts of molecules are essentially identical, having a transoid (D_{2d}) arrangement of the bridging ligands, Mo–Mo bond lengths of 2.097 (3) and 2.093 (2) Å, and two axially coordinated THF molecules with average Mo–O distances of 2.58 (1) and 2.62 (1) Å. Molecules of **2** and **3** also have the transoid arrangement of bridging ligands with Mo–Mo distances of 2.101 (1) and 2.102 (1) Å and one axially coordinated pyridine (Mo–N = 2.563 (8) Å or 4-picoline (Mo–N = 2.592 (8) Å), respectively.

Introduction

Recent investigations in this laboratory of $Cr_2[RNC(R')O]_4\cdot L_2$ compounds[1-3] have shown that ligands of the type RNC(R′)O favor short metal–metal bonds and a marked sensitivity toward axial coordination. For comparison we have prepared and structurally characterized some analogous axially coordinated dimolybdenum compounds. Previous studies have suggested that dimolybdenum compounds, unlike their chromium analogues, do not in general accept axial ligands, although there are exceptions such as $Mo_2(S_2CR)_4\cdot 2THF$.[4,5] However, the recent preparation of $Mo_2[(xylyl)NC(H)O]_4\cdot THF$[6] (xylyl = 2,6-dimethylphenyl) has lead us to believe that, as in the chromium analogues, ligands of the type RNC(R′)O enhance the sensitivity of the Mo_2^{4+} unit toward axial ligands. In order to examine this possibility in more detail, we have undertaken the preparation of additional examples of axially coordinated dimolybdenum compounds. We present a report of the successful preparation and structural characterization of three such derivatives, $Mo_2[(xylyl)NC(CH_3)O]_4\cdot 2THF$ (**1**) and $Mo_2[(xylyl)NC(CH_3)O]_4\cdot L$, $L = NC_5H_5$ (**2**) and $NC_5H_4(p\text{-}CH_3)$ (**3**).

Experimental Section

2,6-Dimethylacetanilide was prepared from acetic anhydride and 2,6-xylidine. After recrystallization from ethanol, the compound had the literature melting point of 176 °C. All manipulations were carried out under an atmosphere of dry argon.

Preparation of $Mo_2[(xylyl)NC(CH_3)O]_4\cdot 2THF$ (1). A solution of $Li[(xylyl)NC(CH_3)O]$ was prepared by dissolving 0.65 g (4 mmol) of 2,6-dimethylacetanilide in 25 mL of THF and adding the corresponding amount of *n*-butyllithium in hexane. The presence of any excess *n*-BuLi is indicated by the appearance of a yellow tint in the reaction mixture. Anhydrous dimolybdenum tetraacetate (0.42 g, 1 mmol) was added to this solution, and the solution was stirred for ~16 h at room temperature. Subsequent filtration gave a yellow solution. Slow evaporation of this solution with a continuous flow of argon produced a good crop of air-sensitive crystals with dimensions up to 1 mm.

Preparation of $Mo_2[(xylyl)NC(CH_3)O]_4\cdot L$, L = Pyridine (2) or 4-Picoline (3). The reaction of 0.04 mol of $Li[(xylyl)NC(CH_3)O]$ with 0.01 mol of $Mo_2(O_2CCH_3)_4$ was carried out as described above. After 10 h the reaction mixture was filtered and the solvent stripped from the yellow filtrate to leave a yellow solid residue. This residue was heated (130 °C) in vacuum (0.05 torr) for 8 h and then dissolved in benzene (30 mL). After filtration of this solution, pyridine or 4-picoline (0.5 mL, 0.06 mol) was added and it was allowed to stand quietly for 10 days. In each case 5–10 mg of well-formed crystals suitable for X-ray diffraction were obtained.

X-ray Data Collection. Suitable crystals of the compounds were coated with epoxy cement, sealed in thin glass capillaries, and mounted on an Enraf-Nonius CAD-4F automatic diffractometer. Intensity data were collected by using Mo Kα radiation ($\lambda_{\bar{\alpha}} = 0.71073$ Å) monochromatized by a graphite crystal in the incident beam. The

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