chemical interactions with a substrate will be the key to photoelectrocatalytic reactions of interest to solar energy conversion.

Acknowledgment. This work was supported by the Advanced Energy Projects Division of the Office of Basic Energy Sciences, Office of Energy Research, United States Department of Energy. J.A.T. acknowledges support from the Division of Chemical Sciences. We also acknowledge Macintosh for work processing and graphics.

Registry No. PdPS, 11083-63-9; $Fe(CN)_6^{4-}$, 13408-63-4; $Fe(CN)_6^{3-}$, 13408-62-3.

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^{13}C NMR Characterization of Nickel(II)-bis(*o*-hydroxynaphthaldimine) Complexes

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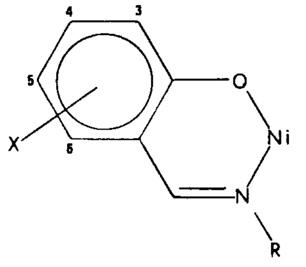
Received November 16, 1983

^{13}C NMR spectra of the complexes bis[1-((((*S*)-1-methylpropyl)imino)methyl)-2-naphtholato]nickel(II) (**1**) and bis[1-((((*R*)-1,2,2-trimethylpropyl)imino)methyl)-2-naphtholato]nickel(II) (**2**) have been obtained in mixed solvents (3:1 v/v) $CHClF_2/CDCl_3$ and $CHClF_2/CD_2Cl_2$, respectively, in the temperature range −30 to −100 °C. For **1**, the temperature dependence of the ^{13}C chemical shifts is affected by a shift to the right at lower temperatures of the tetrahedral ⇌ planar equilibrium. For the largely planar complex **2** ($\mu = 0.55\ \mu_B$), the existence of the following equilibria has been established in solution: umbrella *RR*(δδ) ⇌ stepped *RR*(δλ) ⇌ umbrella *RR*(λλ). Two separate signals for the umbrella diastereoisomers are observed at −40 °C from which a molar fraction of 0.94 for the *RR*(δδ) umbrella form is calculated.

Introduction

Four-coordinate bis-bidentate Schiff base complexes, I, exhibit the equilibria expressed in eq 1[1] in noncoordinating solvents. The



I

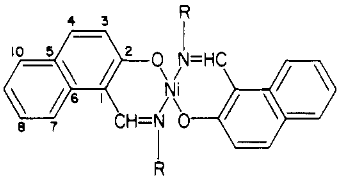
$$\text{polymer(paramagnetic)} \rightleftharpoons \text{monomer(planar diamagnetic)} \rightleftharpoons \text{monomer(tetrahedral paramagnetic)} \quad (1)$$

conformations of chiral complexes of this type, which are of interest in catalysis,[2] have been studied by means of circular dichroism spectroscopy.[3] In the solid state, planar nickel(II) Schiff base complexes have been found in a "stepped" centrosymmetric conformation.[4] Due to the nonplanarity of the chelate rings in solution, two other chiral "umbrella" conformations are possible. (Figure 1). The existence of the equilibrium (2), in which δ and

$$\text{umbrella } (\delta\delta) \rightleftharpoons \text{stepped } (\delta\lambda) \rightleftharpoons \text{umbrella } (\lambda\lambda) \quad (2)$$

λ represent the chirality of the single chelate ring, has been proposed.[3c] The position of the equilibrium (2) depends on the asymmetric induction exerted by the chiral carbon atom of the R substituent (R = chiral group), whose conformational properties are of importance because of the use of such complexes as models for biological systems.[5]

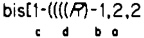
The complexes bis[1-((((S)-1-methylpropyl)imino)methyl)-2-naphtholato]nickel(II) (**1**) and bis[1-((((R)-1,2,2-trimethylpropyl)imino)methyl)-2-naphtholato]nickel(II) (**2**) have been investigated by means of variable-temperature ^{13}C NMR with the hope of understanding their conformational changes in solution.[6]



1 = bis[1-((((*S*)-1-methylpropyl)imino)methyl)-2-naphtholato]nickel(II);

$$R = \overset{c}{C}H\overset{d}{C}H_3\overset{b}{C}H_2\overset{a}{C}H_3$$

2 = bis[1-((((*R*)-1,2,2-trimethylpropyl)imino)methyl)-2-naphtholato]nickel(II);



$$R = \overset{c}{C}H\overset{d}{C}H_3\overset{b}{C}(\overset{a}{C}H_3)_3$$

Experimental Section

Preparation of Compounds. 2-Hydroxy-1-naphthaldehyde (Fluka) was purified on a silica gel column, with $CHCl_3$ as eluent. (+)-(*S*)-2-aminobutane (bp 63 °C; $[\alpha]^{25}{}_D = 7.22°$; optical purity 89%) and (−)-(*R*)-2-amino-3,3-dimethylbutane (bp 100–101 °C; $[\alpha]^{25}{}_D = -4.9°$; optical purity 76%) were prepared according to the methods reported in literature.[7,8]

Compounds **1** and **2** were synthesized by using previously reported procedures:[1,3c] a higher purity for **2** was obtained by using benzene rather than ethyl alcohol as solvent. A solution of (hydroxynaphthalenecarbaldehydato)nickel(II) (2.5 g) in benzene containing (−)-(*R*)-2-amino-3,3-dimethylbutane (3 cm^3) was refluxed in a flask equipped with a Dean–Stark apparatus for 4 h. The solvent was then removed in vacuo,

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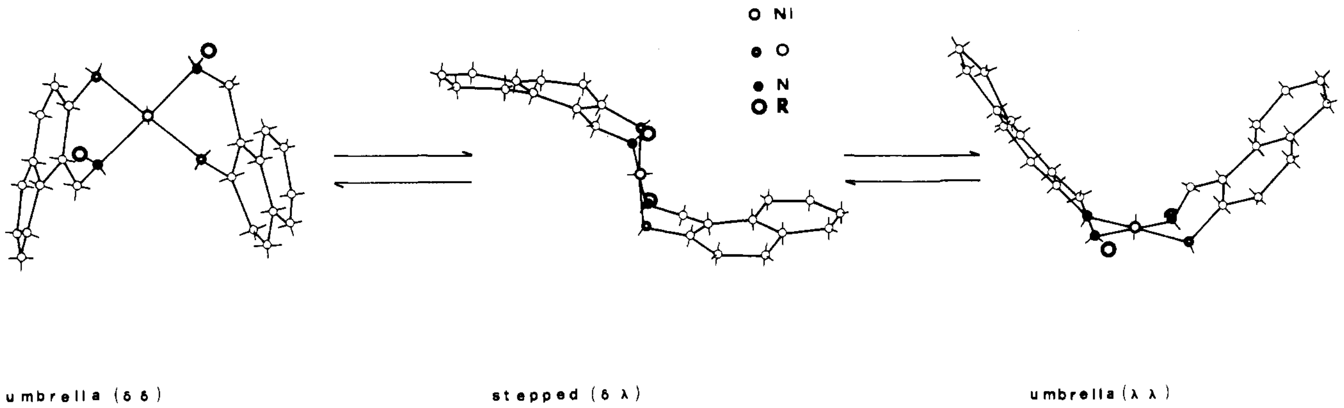

Figure 1. Conformation in solution for a planar and unassociated molecule of the four-coordinate chelate complex of Ni(II).

Table I. ^{13}C NMR Data for **1** and **2** (Chemical Shifts in ppm from Me_4Si)

carbon	**1**	free amine[a]	carbon	**2**	free amine[b]
C[c]	140.08		C(2)	210.53	
C[c]	133.74		C(az)	190.53	
C[c]	132.96		C(1,4)	140.72	
C[c]	127.08		C(8)	129.55	
C[c]	124.40		C(10)	126.19	
C[c]	123.13		C(6)	123.41	
C[c]	122.64		C(7)	116.14	
			C(9)	113.91	
			C(3)	106.65	
			C(5)	94.36	
C(c)	85.90	47.29	C(c)	63.40	54.97
C(b)	42.00	31.75	C(b)	36.50	33.55
C(d)	36.50	22.31	C(a)	28.10	25.36
C(a)	11.60	9.34	C(d)	17.60	17.60

[a] 2-Aminobutane. [b] 3,3-Dimethylbutane. [c] Chemical shifts of aromatic carbon atoms not assigned; see text.

and the dry product was purified by extraction with anhydrous pentane on a Soxhlet apparatus. Both compounds were prepared under nitrogen atmosphere. The magnetic moments in benzene solution were $\mu_t = 1.21$ μ_B for **1** and $\mu_t = 0.55$ μ_B for **2**. Anal. Calcd for **1**, $C_{30}H_{32}N_2O_2Ni$ (mp 153–154 °C): C, 70.51; H, 6.26; N, 5.48. Found: C, 70.34; H, 6.16; N, 5.50. Calcd **2**, $C_{34}H_{40}O_2N_2Ni$ (mp 177–179 °C) C, 71.95; H, 7.10; N, 4.93. Found: C, 71.54; H, 7.40; N, 4.93.

NMR Measurements. The ^{13}C NMR spectra were recorded on a CFT-20 spectrometer and on an XL-100 spectrometer, both with standard variable-temperature equipment. Me_4Si was used as an internal reference. The spectra at 37 °C were obtained in CD_2Cl_2 and $CDCl_3$, while those at −20 to −90 °C were obtained in CCl_3F and $CHClF_2/CD_2Cl_2$. Operating conditions: full proton decoupling; pulse width 9 μs; pulse delay 0.8 s; number of scans 2000; concentration of samples 0.9 M in a mixture of $CHClF_2/CD_2Cl_2$ (3:1 v/v) or $CHClF_2/CDCl_3$; 8-mm spinning tubes. The tubes were carefully degassed by several freeze–thaw cycles under high vacuum before sealing. $CHClF_2$ was transferred under high vacuum to CD_2Cl_2 or $CDCl_3$ solution in the NMR tube. The molar fraction was calculated from the areas of the two peaks at 62.11 and 71.34 ppm in the spectrum at −40 °C without nuclear Overhauser effect.

Results

The ^{13}C NMR chemical shifts of compounds **1** and **2** at 37 °C are listed in Table I. Compound **1** exhibits an aromatic pattern with only seven signals; assignment of all the carbon resonances of the aromatic rings is not possible.

Assignments of aromatic carbon resonances of **2** are proposed on the basis of single-frequency off-resonance ^1H-decoupling experiments to distinguish between carbon atoms with and without hydrogen atoms bonded to them. Additionally, the assignments of **2** are based on the chemical-shift theory since it is a system of the odd-alternate type. Finally, assignments are also based on changes in signal intensity at lower temperatures.[9] The assignments are certain for C(2), C(az), C(1), and C(5), while reverse assignments are possible for C(8), C(10), C(7), and C(9). In both complexes the ^{13}C resonances of the aliphatic substituent are deshielded with respect to those of the free ligand, as expected for a not completely diamagnetic planar complex. The tetrahedral structure at the metal affects the nearest carbon atoms. This effect decreases with distance. The deshielding and broadening (due to dipolar nuclear–electronic relaxation) proved very strong for diastereotopic carbon atoms, particularly CH(c) in **1**, in which $\mu_t = 1.21$ μ_B.

Table II. Δx_i[a] Values for Carbon Atoms in the Complexes

	Δx_i (+20 °C)		Δx_i (−70 °C)
carbon	**1**	**2**	**1**
C(a)	2.26	2.74	2.26
C(b)	11.05	2.95	1.85
C(c)	**38.61**	**8.43**	**16.90**
C(d)	14.19	0.0	2.99

[a] $\Delta x_i = \delta_c(\text{complex}) - \delta_c(\text{amine})$.

Variable-Temperature Studies

Complex 1. In the variable-temperature experiment all carbon atoms are shifted to high field, especially CH(c) (Figure 2a), and the spectra reveal the same pattern down to −90 °C. The differences in chemical shift (Δx_i) between the carbon atoms of the alkyl chain in the complex at experimental temperature and those in the corresponding free amine at 20 °C are given in Table II.

Complex 2. The behavior of the chemical shift at variable temperature for the aliphatic carbon atoms is shown in Figure 2b; the values of the chemical shifts for the aromatic carbons of **2** are reported in Table III and Δx_i values in Table II. The observed ^{13}C spectrum of the aliphatic (a) and aromatic (b) carbons at −20 and −70 °C are shown in Figure 3. A small signal appears to the left of the CH(c) signal on decreasing the temperature. The new signal increases in intensity from −40 to −70 °C and becomes even more intense at −90 °C (Figure 4). The same behavior is observed for $CH_3(d)$, C(b), and the aromatic signals C(2), C(az), C(4), C(9), C(7), C(3), and C(5). The greatest differences in chemical shift between the signals were observed for CH(c), $CH_3(d)$, C(az), C(1), and C(3).

Discussion

All the carbon atoms in the ^{13}C NMR spectra are shifted to high field at lower temperatures due to shift of the tetrahedral ⇌ planar equilibrium to the right.[10] This is accompanied by a decrease in the width of the resonance signals, particularly CH(c). Appreciable molecular association, eq 1, is excluded since polymeric forms should give broadening and deshielding. Furthermore, complex **1** exhibits an appreciable displacement of the equilibrium

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(10) The symbols *SS* or *RR* indicate the chirality of the asymmetric carbon atoms of the alkyl substituent.

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Table III. ^{13}C NMR Data for **2** (Chemical Shifts in ppm from Me_4Si)

carbon	−30 °C	−40 °C	−60 °C	−70 °C	−90 °C	−100 °C	−120 °C	−70 °C[a]
C(2)	210.53		208.29 207.74	208.85 207.74	207.74 207.18	208.29 207.18	208.29 207.18	1.11
C(az)	190.43	189.31 187.63	189.23 187.63	189.23 187.91	189.86 187.63	189.31 187.63	189.31 187.63	1.95
C(1)	140.72	141.27 140.16	141.83 140.16	141.83 140.16	141.27 139.60	141.27 139.60	141.27 139.60	1.67
C(4)	113.91	114.47	114.47	115.02 114.47	115.02 114.40	115.02 114.47		0.55
C(3)	106.65	107.76 106.93	108.32 106.65	108.32 106.93	108.32 106.65	108.32 106.93	107.76 106.65	1.39
C(5)	94.36	96.02	95.48	96.04 95.48	96.04 94.92	96.04 94.92	95.48 94.36	0.55

[a] Difference of chemical shift at −70 °C between signals.

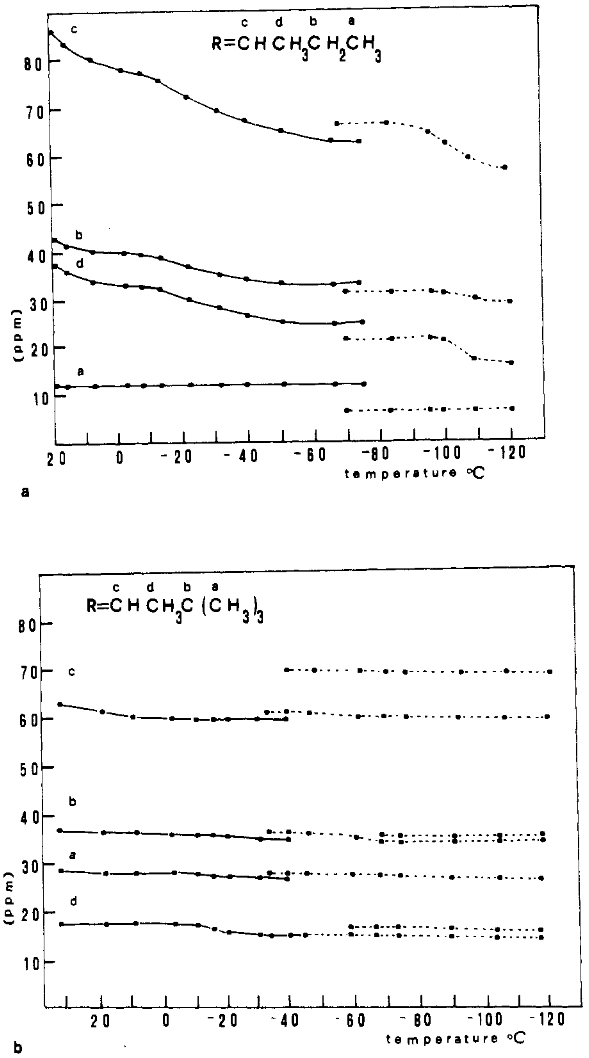

Figure 2. Temperature-dependent chemical shift of aliphatic carbon atoms for (a) complex **1** ((—) CD_2Cl_2, (- - -) $CHClF_2/CDCl_3$ (3:1 v/=)) and (b) complex **2** ((—) CD_2Cl_2, (- - -) $CHClF_2/CD_2Cl_2$ (3:1 v/v)).

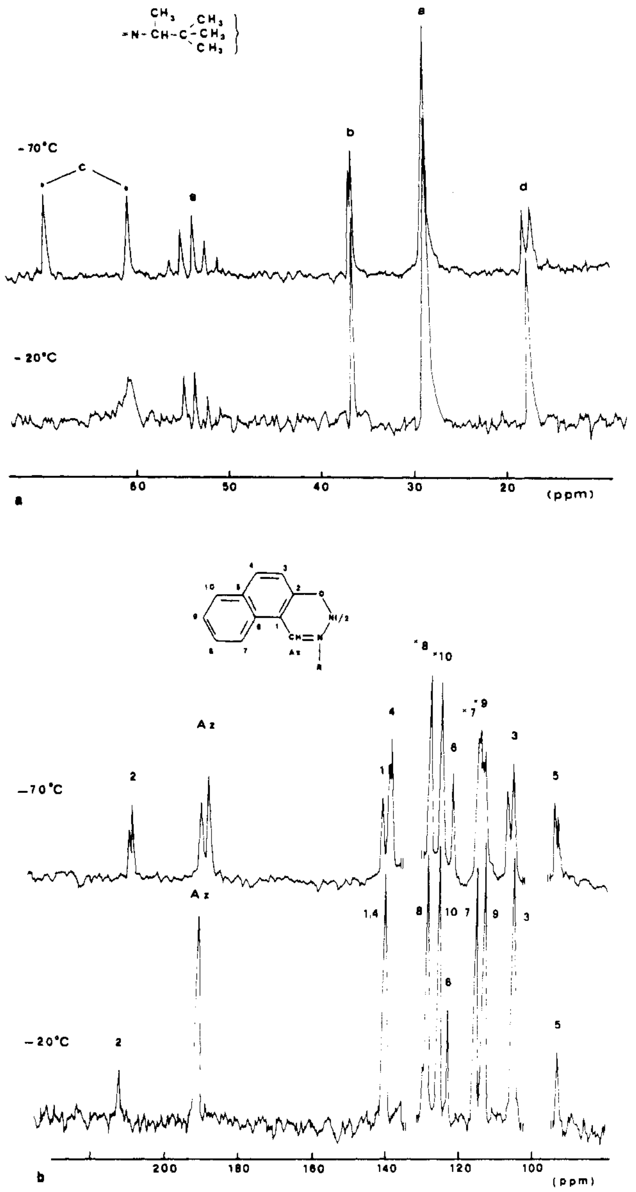

Figure 3. ^{13}C spectra of (a) aliphatic and (b) aromatic carbon atoms of **2** at −70 and −20 °C.

(1) to the right at lower temperature. The differences in chemical shift at −70 °C between the aliphatic carbon atoms of the complex and the amine are shown in Table II; it can be seen that the effect of complexation at this temperature for **1** (which at room temperature has $\mu_t = 1.21\ \mu_B$) is about the same as that presented at 20 °C by complex **2** (which at this temperature has $\mu_t = 0.55\ \mu_B$). Due to the tetrahedral $\rightleftharpoons$ planar interconversion at −90 °C, a temperature analysis of **1** in equilibrium 2 is impossible.

The largely planar complex **2**, on the other hand, provides a good example for analyzing equilibrium 2 in solution. At slow exchange, each carbon atom should present four signals: one each for the umbrella forms (*RR*($\delta\delta$), *RR*($\lambda\lambda$) (C_2)) and two for the stepped form. In the stepped form, the two signals are due to the asymmetric structure of this species (C_1). Signals for the umbrella form should be of different intensity, depending on the conformer/conformer ratio, while those of the stepped form should be of equal intensity. The spectrum shows a rather wide signal at about 60 ppm, which at −40 °C changes slightly its chemical shift, with

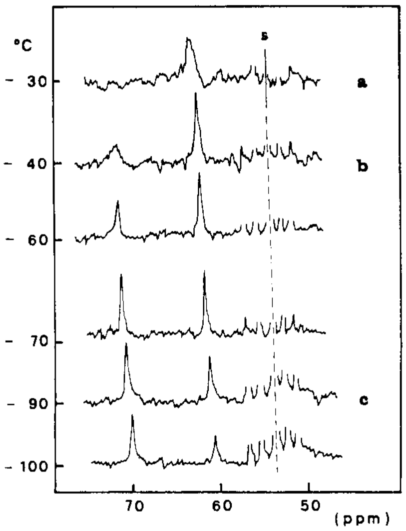

Figure 4. Temperature-dependent 20-MHz ^{13}C spectra for carbon atom CH(c) of **2** in $CHClF_2/CD_2Cl_2$ (3:1 v/v) at (a) -30 °C (near coalescence), (b) -40 °C (slow-exchange limit), and (c) -90 °C (inversion of conformer/conformer ratio).

a new small signal appearing to its left. Analysis is complex because the exchange is over three sites, and the exchange shows variation of population with temperature.

Our interpretation of the phenomenon is that at room temperature there is an averaged signal coming from the exchange between the three sites $RR(\delta\delta)$, stepped $RR(\delta\lambda)$, and umbrella $RR(\lambda\lambda)$, with the equilibrium strongly shifted toward an umbrella form. At -40 °C we have the separation of the two diastereoisomers umbrella $RR(\delta\delta)$ and umbrella $RR(\lambda\lambda)$: two signals rise by these two diastereoisomers in slow equilibrium. The signals are of different intensity, showing the existence of a prevailing umbrella conformation, in agreement with the results of previous CD studies.[3c] As far as the stepped form is concerned, separate signals of equal intensity between the lines corresponding to the two umbrella forms are not observed in the ^{13}C NMR spectrum. Possibly, there may be a signal of the "stepped" conformer under each "umbrella" line.

A molar fraction of 0.94 of the $RR(\delta\delta)$ umbrella form is calculated[12] because the stepped form, if present, would contribute one signal under each peak of the umbrella form in equal intensity. The prevalence of this diastereoisomer should increase at lower temperature. On the contrary, an inversion of the population ratio is observed upon further lowering the temperature (Figure 4). This inversion is observed only with $CHClF_2$ while CCl_3F, $CHCl_2F$, or a mixture of them does not give this inversion. Several authors[13] have reported a marked solute-solvent interaction in experiments with fluorinated solvents, in particular when there is a group like *tert*-butyl, which may account for our observations.

Registry No. **1**, 56647-30-4; **2**, 98574-19-7.

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(12) This calculation can be done by starting from the area of the two peaks at 62.11 and 71.34 ppm in the ^{13}C NMR spectrum of **2** at 40 °C, without the nuclear Overhauser effect.

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Synthesis and Properties of *cis*-Bis(dinitrogen)tetrakis(trimethylphosphine)tungsten(0). Crystal and Molecular Structures of $[W(N_2)(PMe_3)_5]$ and *trans*-$[W(C_2H_4)_2(PMe_3)_4]$

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Received March 25, 1985

The dispersed-sodium reduction of $WCl_4(PMe_3)_3$ in tetrahydrofuran under nitrogen gives *cis*-$[W(N_2)_2(PMe_3)_4]$ (**1**), which upon reaction with PMe_3 under argon, at 40-50 °C, affords $[W(N_2)(PMe_3)_5]$ (**2**). If $WCl_4(PMe_3)_3$ is reduced with sodium amalgam in ethylene-saturated tetrahydrofuran, *trans*-$[W(C_2H_4)_2(PMe_3)_4]$ (**3**) is formed. Complex **3** can also be obtained by reaction of **1** with C_2H_4 under UV light. Reaction of **3** with CO (1 atm) yields *trans,mer*-$[W(C_2H_4)_2(CO)(PMe_3)_3]$ (**4**), while with 2-3 atm of CO *trans,trans,trans*-$[W(C_2H_4)_2(CO)_2(PMe_3)_2]$ (**5**) is obtained. The molybdenum analogue of the latter complex, *trans,trans,trans*-$[Mo(C_2H_4)_2(CO)_2(PMe_3)_2]$ (**6**), has been similarly prepared. Compounds **2** and **3** have been studied by X-ray crystallography and found to be isostructural with their corresponding molybdenum analogues. $[W(N_2)(PMe_3)_5]$ (**2**) is orthorhombic, *Pnma*, with unit cell constants $a = 21.990$ (6) Å, $b = 12.108$ (3) Å, $c = 9.722$ (2) Å, and $D_{calcd} = 1.52$ g cm^{-3} for $Z = 4$. **2** was refined to a conventional *R* value of 0.041 by using 1753 independent observed reflections. The tungsten atom resides on a crystallographic mirror plane, and a W-N bond length of 2.04 (2) Å is observed. *trans*-$[W(C_2H_4)_2(PMe_3)_4]$ (**3**) crystallizes in the monoclinic space group $P2_1/n$ with $a = 10.130$ (3) Å, $b = 13.699$ (4) Å, $c = 17.029$ (6) Å, $\beta = 98.84$ (2)°, and $D_{calcd} = 1.53$ g cm^{-3} for $Z = 4$. The final *R* value based on 1465 reflections is 0.028. The two ethylene groups are trans and mutually perpendicular. The average W-C and W-P bond separations are 2.26 (1) and 2.48 (1) Å, respectively.

Introduction

The chemistry of dinitrogen complexes of molybdenum and tungsten continues to attract much attention and to produce new and exciting results. Although much of the activity in this area is devoted to studies related to mimicking the function of nitrogenase,[2] a great deal of effort has been dedicated to the search for novel types of complexes and modes of dinitrogen coordination and to the study of the new reaction chemistry of these interesting species. The recent characterization of a tungsten-aluminum complex[3] containing a triply end-on-bridged dinitrogen ligand, the synthesis and structural determination of the tris(dinitrogen) complex *mer*-$[Mo(N_2)_3(P\text{-}n\text{-}Pr_2Ph)_3]$,[4] and the formation of η^6-pyridine[5] and bis(carbon dioxide)[6] derivatives of molybdenum(0) may be noted among the many significant contributions reported in this field in the last few years.

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