teractions are $\sigma^*_{CF}-\sigma^*_{CX}$ (for $^{19}F$) and $\sigma_{CSn}-\sigma^*_{CX}$ (for $^{119}Sn$); however, we do not have a simple interpretation of their mode of action on the shifts since there are no model systems from which parallels can be drawn. It is possible that these orbital interactions may significantly govern the average excitation energy term ($\Delta E$) in the expression for the dominant paramagnetic contribution to the shifts of both probe nuclei ($\Delta E = \sigma_{CF} \rightarrow \sigma^*_{CF}$ (for $^{19}F$) and $\sigma_{CSn} \rightarrow \sigma^*_{CSn}$ (for $^{119}Sn$)).[18] The different relative magnitude of the "residual" contributions for both probes ($^{19}F$[7] and $^{119}Sn$) in the bicyclo[2.2.2]octane ring system probably reflects the different nature of the orbital interactions underlying the electron-delocalization mechanisms for both probes as well as their mix.

These and additional features of this work will be reported in full at a later date.

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**Registry No.** 2 (X = CN), 84010-79-7; 2 (X = F), 78385-88-3; 2 (X = Cl), 84010-80-0; 2 (X = Br), 84010-81-1; 2 (X = I), 84010-82-2; 2 (X = $N(CH_3)_2$), 84010-83-3; 2 (X = OMe), 84010-84-4; 2 (X = $C_6H_5$), 68756-27-4; 2 (X = $p$-$FC_6H_4$), 68756-25-2; 2 (X = $CH_3$), 84010-85-5; 2 (X = $C(CH_3)_3$), 84010-86-6; 2 (X = $Sn(CH_3)_3$), 84010-87-7; 3 (X = $OCH_3$), 84010-88-8; 3 (X = F), 84010-89-9; 3 (X = I), 84010-90-2; 3 (X = $Sn(CH_3)_3$), 84010-91-3.

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[18] As X becomes more electronegative, both the $\sigma^*_{CF}-\sigma^*_{CX}$ and $\sigma_{CSn}-\sigma^*_{CX}$ orbital interactions will *increase* and, hence, lead to a decrease and increase, respectively, in $\Delta E$ for $^{19}F$ and $^{119}Sn$ chemical shifts, i.e., downfield (for $^{19}F$) and upfield (for $^{119}Sn$) contributions for the through-space effect, as observed.

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# Oxidative Additions to $(W{\equiv}W)^{6+}$ Centers: The Influence of Lewis Base Association Reactions

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Oxidative-addition reactions have been extensively studied in mononuclear organometallic chemistry since they represent one of the key steps in many catalytically important reactions.[1] Oxidative addition occurs to coordinatively unsaturated metal centers, and thus Lewis base association or dissociation steps may influence the overall rate of reaction. This is well exemplified by the studies of molecular hydrogen addition to Wilkinson's compound, $RhCl(PPh_3)_3$[2] and is generally true for oxidative-addition reactions involving phosphine complexes of the group 8 transition elements.[3] We here show that a parallel situation occurs in dinuclear transition-metal chemistry.

(1) $W_2(NMe_2)_6$ (M≡M) has been previously shown[4] to react with $i$-PrOH to give the tetranuclear complex $W_4(\mu\text{-}H)_2(O\text{-}i\text{-}Pr)_{14}$. The reaction was proposed to proceed in three stages: (i) alcoholysis, $W_2(NMe_2)_6 + i\text{-PrOH} \rightarrow W_2(O\text{-}i\text{-}Pr)_6 + HNMe_2$; (ii) oxidative addition, $W_2(O\text{-}i\text{-}Pr)_6 + i\text{-PrOH} \rightarrow W_2(H)(O\text{-}i\text{-}Pr)_7$ (M=M); (iii) dimerization by RO bridge formation, $2W_2(H)(O\text{-}i\text{-}Pr)_7 \rightarrow W_4(H)_2(O\text{-}i\text{-}Pr)_{14}$. We have now found that $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$ can be isolated from the reaction between $W_2(NMe_2)_6$ and $i$-PrOH in hexane at 0 °C as a yellow crystalline compound.[5] The molecular structure deduced from an X-ray study[6] shows that the $HNMe_2$ ligands complete roughly square-planar coordination sites at each tungsten. The overall $W_2O_6N_2$ moiety has virtual $C_2$ symmetry, and the two $WO_3N$ units are nearly eclipsed as a result of hydrogen bonding, N–H···OR, across the W≡W bond. $^1H$ NMR studies show that below 0 °C in toluene-$d_8$ the $HNMe_2$ ligands are tightly bound, and the $^1H$ NMR spectra are consistent with expectations based on the solid-state molecular structure. At ambient temperatures, the $HNMe_2$ ligands are labile according to the generalized equation (1) and may readily be exchanged for ligands that co-

$$W_2(OR)_6L_2 \rightleftharpoons W_2(OR)_6 + 2L \qquad (1)$$

ordinate more strongly such as pyridine, $PMe_3$, and $Me_2PCH_2CH_2PMe_2$.[7] However, at 0 °C the $HNMe_2$ ligands are sufficiently tightly bound to prevent reaction with excess $i$-PrOH.

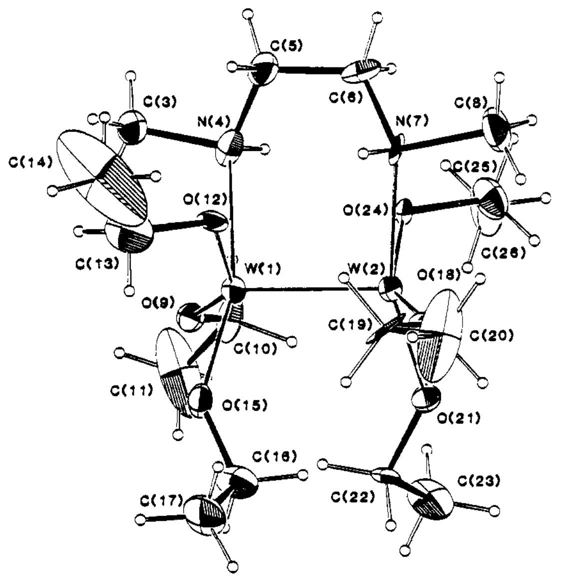

**Figure 1.** ORTEP view of the $W_2(OEt)_6(Me(H)NCH_2CH_2N(H)Me)$ molecule. Atoms are represented as ellipsoids drawn to include 20% probability of thermal displacement. Some pertinent bond distances (Å) and angles (deg) are as follows: W(1)–W(2) = 2.296 (2), W(1)–O(9), –O(12), –O(15), –N(4) = 1.97 (2), 1.96 (2), 1.88 (2), 2.26 (2); W(2)–O(18), –O(21), –O(24), –N(7) = 1.89 (2), 1.90 (2), 1.95 (2), 2.31 (2); W(2)–W(1)–O(9), –O(12), –O(15), –N(4) = 106.0 (5), 101.2 (5), 106.8 (5), 90.0 (5); W(1)–W(2)–O(18), –O(21), –O(24), –N(7) = 104.1 (5), 106.9 (5), 98.7 (4), 91.3 (4).

(2) $W_2(NMe_2)_6$ (M≡M) has been shown[8] to react with EtOH and MeOH according to eq 2. The tetranuclear complex may

$$2W_2(NMe_2)_6 + 16ROH \rightarrow W_4(OR)_{16} + 2H_2 + 12HNMe_2 \qquad (2)$$

be viewed as the dimerized product of $W_2(OR)_8$ (M=M).[9] Irrespective of the detailed pathway of the formation of $W_4(OEt)_{16}$, tungsten has been oxidized from oxidation state 3+ to 4+ in reaction 2.

In marked contrast, when $W_2(NMe_2)_6$ is allowed to react with EtOH in hexane in the presence of $Me(H)NCH_2CH_2N(H)Me$ at room temperature, oxidative addition does not occur and the

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[1] Tolman, C. A. *Chem. Soc. Rev.* **1972**, *1*, 337.

[2] Tolman, C. A.; Meakin, P. Z.; Lindner, D. L.; Jesson, J. P. *J. Am. Chem. Soc.* **1974**, *96*, 2762.

[3] Tolman, C. A.; Faller, J. W. In "Homogeneous Catalysis with Metal Phosphine Complexes"; Plenum Press: New York, in press.

[4] Akiyama, M.; Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Haitko, D. C.; Leonelli, J.; Little, D. *J. Am. Chem.* **1981**, *103*, 779.

[5] Standard procedures for the handling of oxygen and moisture-sensitive materials were used throughout. Satisfactory elemental analyses have been obtained for all the new compounds reported.

[6] Indiana University, MSC Report No. 82018.

[7] The preparation and full structural characterization of $W_2(O\text{-}i\text{-}Pr)_6(py)_2$ has been reported: Akiyama, M.; Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Haitko, D. A.; Little, D.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 2266. The phosphine complexes are prepared by phosphine displacement of $HNMe_2$ in $M_2(OR)_6(HNMe_2)_2$ compound where R = $i$-Pr or $CH_2$-$t$-Bu. Chetcuti, M. J.; Chisholm, M. H.; Stewart, J., results to be published.

[8] Chisholm, M. H.; Huffman, J. C.; Kirkpatrick, C. C.; Leonelli, J. *J. Am. Chem. Soc.* **1981**, *103*, 6093.

[9] Cf. $Mo_2(O\text{-}i\text{-}Pr)_8$ (M=M). Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Reichert, W. W. *Inorg. Chem.* **1978**, *17*, 2944.

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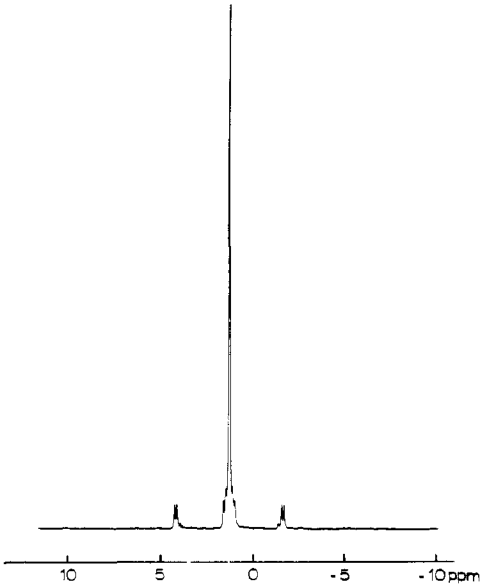

**Figure 2.** $^{31}P$ NMR spectrum (40.5 MHz, 25 °C, toluene-$d_8$ solvent) of $W_2(OCH_2\text{-}t\text{-}Bu)_6(PMe_3)_2$. Chemical shift $\delta$ 1.5 relative to external $H_3PO_4$ (85% aq); $^1J_{^{183}W-^{31}P} = 240$ Hz, $^2J_{^{183}W-^{31}P} = 20$ Hz, $^3J_{^{31}P-^{31}P} = 5.4$ Hz.

chelated amine adduct $W_2(OEt)_6(Me(H)NCH_2CH_2N(H)Me)$ is isolated as a red-orange crystalline compound.[5] The molecular structure deduced from an X-ray study[10] shows that the chelated amine straddles the $W\equiv W$ bond so that the molecule has virtual $C_2$ symmetry and the two ends of the molecule are almost perfectly staggered (see Figure 1). In solution, the diamine is tightly bound and not easily replaced by other donor ligands. The $^1H$ NMR spectrum in toluene-$d_8$ shows three types of OEt ligands: each ethyl group appears as an $ABX_3$ spectrum. The $^1H$ NMR signals associated with the chelated amine also indicate a rigid structure. Evidently, enantiomerization is not rapid on the NMR time scale, and the diamine, which is firmly coordinated, denies EtOH access to the $(W\equiv W)^{6+}$ center, which is necessary for oxidative addition.

(3) When hydrocarbon solutions of $W_2(NMe_2)_6$ are allowed to react with alcohols in the presence of $PMe_3$ (≥2 equiv) at room temperature, the phosphine adducts $W_2(OR)_6(PMe_3)_2$ are formed (R = *i*-Pr, $CH_2$-*t*-Bu, and Et).[5] The molecular structure of the neopentoxide reveals two roughly square-planar $WO_3P$ units joined by a $W\equiv W$ bond of distance 2.362 (2) Å. The conformation is staggered with the P–W–W–P torsion angle of 114°. In solution, rotation about the $W\equiv W$ bond is rapid on the $^1H$ NMR time scale and the $PMe_3$ ligands are tightly bound as evidenced by $J_{^{183}W-^{31}P}$ and $J_{^{31}P-^{31}P}$ couplings (see Figure 2).

(4) Addition of pivalic acid, *t*-BuCOOH, which is a much stronger acid than either *i*-PrOH or EtOH and is known to oxidize tungsten(0) to the 4+ oxidation state in reactions involving $W(CO)_6$,[12] reacts smoothly with $W_2(O\text{-}t\text{-}Bu)_6$ in hydrocarbon solvents to give $W_2(O_2C\text{-}t\text{-}Bu)_6$, which may be isolated as a yellow crystalline solid.[5] This compound has not been structurally characterized by an X-ray study because its spectroscopic properties indicate a structure analogous to that found for $W_2(O_2CNMe_2)_6$.[13] In the mass spectrometer, the ion of highest mass corresponds to $W_2(O_2C\text{-}t\text{-}Bu)_6^+$ and many daughter $W_2$-containing ions are observed. The $^1H$ NMR spectrum shows three types of methyl signals in the integral ratio 1:1:1.

In the reaction between $W_2(O\text{-}t\text{-}Bu)_6$ and *t*-BuCOOH, each replacement of an alkoxy ligand by a carboxylate group allows an increase in coordination number of one if the carboxylate group acts as a bidentate ligand. The intermediate $W_2(O\text{-}t\text{-}Bu)_4(O_2C\text{-}t\text{-}Bu)_2$ in the formation of $W_2(O_2C\text{-}t\text{-}Bu)_6$ probably has a structure akin to that found for $M_2(O\text{-}t\text{-}Bu)_4(O_2CO\text{-}t\text{-}Bu)_2$[14] compounds and $Mo_2(O\text{-}t\text{-}Bu)_4(O_2CPh)_2$.[15] In the reactions described in 1–3 above, it is evident that monodentate donors, L, or bidentate donors, L–L, can coordinate to the dinuclear center to give $W_2(OR)_6L_2$ and $W_2(OR)_6(L\text{–}L)$ compounds, and depending upon the relative binding abilities of the ligand, this may either serve to suppress (L = $HNMe_2$, R = *i*-Pr) or completely block (L = $PMe_3$ or L–L = $Me(H)NCH_2CH_2N(H)Me$) the oxidative addition reaction that takes $(W\equiv W)^{6+}$ to $(W{=}W)^{8+}$. The pathway leading to oxidative addition finds a parallel with that noted recently by Nubel and Brown wherein 1,2-$Re_2(CO)_8L_2$ compounds (L = $H_2O$ or pyridine) give $(\mu\text{-}H)Re_2(CO)_8(\mu\text{-}X)$ compounds (X = OH or $C_5H_4N$).[16]

Further studies are in progress.[17]

**Registry No.** $W_2(NMe_2)_6$, 54935-70-5; *i*-PrOH, 67-63-0; EtOH, 64-17-5; $NHMe_2$, 124-40–3; $W_2(OPr\text{-}i)_6(HNMe_2)_2$, 84028-40-0; $PMe_3$, 594-09-2; $W_2(OPr\text{-}i)_6(PMe_3)_2$, 84028-42-2; $W_2(OEt)_6(PMe_3)_2$, 57125-20-9; *t*-BuCOOH, 75-98-9; $W_2(O_2CBu\text{-}t)_6$, 84028-44-4; W, 7440-33-7.

**Supplementary Material Available:** Table of atomic coordinates and thermal parameters for $W_2(OEt)_6(MeN(H)CH_2CH_2N(H)Me)$ (3 pages.) Ordering information is given on any current masthead page. Complete Molecular Structure Center reports are available, in microfiche form only, from the Indiana University Library.

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(10) Crystal data for $W_2(OEt)_6(MeN(H)CH_2CH_2N(H)Me)$ at −61 °C: space group $P2_1/n$, $a = 19.050$ (14) Å, $b = 15.627$ (9) Å, $c = 8.793$ (4) Å, $\beta = 104.27$ (4)°, $Z = 4$, $d_{calcd} = 1.901$ g cm$^{-3}$. Of the 2667 reflections collected with use of Mo K$\alpha$ radiation, $6° \leq 2\theta \leq 40°$, the 1739 reflections having $F > 2.33\ F$ were used in the full-matrix refinement. Due to the excessive thermal parameters, the hydrogen atoms were included as fixed idealized atoms, and no attempt was made to refine them. The final residuals are $R_F$ 0.063 and $R_{wF} = 0.056$.

(11) Indiana University, MSC Report No. 82009.

(12) Bino, A.; Cotton, F. A.; Dori, Z.; Koch, S.; Kuppers, H.; Millar, M. *Inorg. Chem.* **1978**, *17*, 3245.

(13) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Stults, B. R. *Inorg. Chem.* **1977**, *16*, 603.

(14) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Reichert, W. W. *J. Am. Chem. Soc.* **1978**, *100*, 1727.

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(16) Nubel, P. O.; Brown, T. L. *J. Am. Chem. Soc.* **1982**, *104*, 4955.

(17) We thank the Department of Energy, Chemical Science Division, the Wrubel Computing Center, and the taxpayers of the state of Indiana for support.

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## Effect of Nickel(II) and Cobalt(III) and Other Metal Ions on the Racemization of Free and Bound L-Alanine[1]

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The catalytic effects of transition-metal ions on the reactivity of amino acids and their derivatives are well-known.[2] Increased reactivity occurs when metal ions are present with amino acids in base-catalyzed aldol-type condensations,[3] isotope exchange,[4]

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(1) Presented in part at the Fifth IUPAC Conference on Physical Organic Chemistry in Santa Cruz, CA, Aug 17–22, 1980, and in part at the 183rd National Meeting of the American Chemical Society Las Vegas, NV, March 28, 1982. Abstracted from an M.S. Thesis submitted by Awni Khatib to the Graduate School at Utah State University, 1982.

(2) For reviews see: (a) R. D. Gillard, *Inorg. Chim. Acta Rev.*, **1**, 69, (1967); (b) A. E. Martell, In "Metal Ions in Biological Systems", H. Sigel, Ed., Marcel Dekker, New York, 1973, Vol. 2, pp 207–293; (c) A. Pasini and L. Casella, *J. Inorg. Nucl. Chem.*, **36**, 2133, (1974); (d) D. A. Phipps, *J. Mol. Catal.*, **5**, 81 (1979); (e) R. W. Hay and D. R. Williams, in "Amino acids, Peptides and Proteins", Chemical Society, London, 1981, Vol. 11, pp 475–503.

(3) (a) S. Akabori, T. T. Otani, R. Marshall, M. Winitz, and J. P. Greenstein, *Arch. Biochem. Biophys.*, **83**, 1 (1959); (b) R. D. Gillard and P. M. Harrison, *J. Chem. Soc. A*, 1657 (1967); (c) J. P. Aune, P. Maldonado, G. Larcheres, and M. Pierrot, *J. Chem. Soc., Chem. Commun.*, 1351 (1970); (d) J. R. Brush, R. J. Magee, M. J. O'Connor, S. B. Teo, R. J. Geue, and M. R. Snow, *J. Am. Chem. Soc.*, **95**, 2034 (1973); (e) D. A. Phipps, *Inorg. Chim. Acta*, **27**, L103 (1978); (f) L. Casella, A. Pasini, R. Ugo, and M. Visca, *J. Chem. Soc., Dalton Trans.*, 1655 (1980); (g) M. G.-Weller and W. Beck, *Inorg. Chim. Acta*, **57**, 107 (1982).

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