of the structure of karachine (**2**) indicates the degree of complexity attainable in nature starting from a relatively simple berbinoid skeleton.[6]

Acknowledgment. This project was supported by Grant CA-11450 from the National Cancer Institute, NIH, DHHS. G.B. is the recipient of an IREX fellowship. We are grateful to Theresa S. Dunne for technical assistance. A.R. and A.A.A. express their gratitude to Hakim Mohammad Said, Chairman, Hamdard National Foundation, Karachi, for providing the plant material.

Registry No. 2, 80908-02-7; **3**, 80908-03-8.

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(6) For a recent review on purely synthetic adducts of berberine with acetone, see: Govindachari, T. R.; Pai, B. R.; Rajeswari, S.; Natarajan, S.; Chandrasekaran, S.; Premila, M. S.; Charubala, R.; Venkatesan, K.; Bhadbhade, M. M.; Nagarajan, K.; Richter, W. J.; *Heterocycles* **1981**, *15*, 1463. Such adducts bear minimal structural resemblance to karachine.

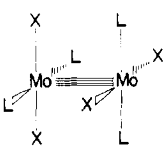
Quadruply Bonded Dimolybdenum Compounds of the Type $Mo_2(O_2CR)_2X_2(PR_3)_2$: Evidence for Kinetic and Structural Trans Effects

Gregory S. Girolami, Vera V. Mainz, and
Richard A. Andersen*

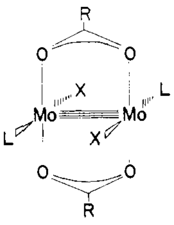
*Department of Chemistry, University of California
Berkeley, California 94720*

Received October 19, 1981

It has been shown recently that the PEt_3 ligands in $Mo_2Me_4(PEt_3)_4$, of stereochemistry I, undergo stepwise exchange with



I



II

either PMe_3 or PMe_2Ph in toluene solution by a dissociative mechanism.[1] In this class of molecules, the phosphine ligands L are cis to the anionic groups X. An analogous study of binuclear compounds in which the phosphines are trans to the anionic groups was of interest. The bis(carboxylato) complexes of stereochemistry II are well suited for such a study.[2-4] We now present kinetic, crystallographic, and spectroscopic data as a function of the anionic group, X, which provide the first evidence for both kinetic and structural trans effects operating in quadruply bonded dimers.

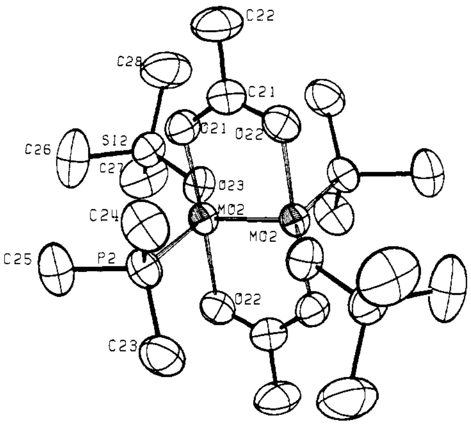


Figure 1. ORTEP view of $Mo_2(O_2CMe)_2(OSiMe_3)_2(PMe_3)_2$. Important bond lengths and angles: Mo–Mo = 2.114 (1) Å, Mo–O(siloxide) = 2.019 (9) Å, Mo–O(acetate) = 2.11 (1) Å, Mo–Mo–P = 94.02 (3)°, Mo–Mo–O(siloxide) = 116.9(5)°, P–Mo–O(siloxide) = 149.0(5)°.

Table I. Magnitudes of $^3J_{PP}$ in the Compounds $Mo_2(O_2CCMe_3)_2X_2(PMe_2Et)(PMe_3)$

X	$^3J_{PP}$, Hz	X	$^3J_{PP}$, Hz
CH_2CMe_3	4	Cl	25
CH_2SiMe_3	6	Br	29
Me	6	$N(SiMe_2H)_2$	33
I	20	$OSiMe_3$	39

The red siloxide derivative $Mo_2(O_2CCMe_3)_2(OSiMe_3)_2(PMe_3)_2$[5] can be prepared from $Mo_2(O_2CCMe_3)_4$, $LiOSiMe_3$, and PMe_3 in diethyl ether, followed by crystallization from pentane at −10 °C. The NMR parameters indicate a structure of type II, and this was confirmed by an X-ray crystallographic study (see Figure 1).[6] The structure has two independent half-molecules in the asymmetric unit. Each molecule contains a crystallographic inversion center, and each molecules possesses nearly C_{2h} symmetry, though the siloxide $SiMe_3$ groups are rotated slightly out of the $Mo_2O_2P_2$ plane, giving Mo–Mo–O–Si torsion angles of 166.0 and 145.6° for the two independent molecules in the unit cell. The overall geometry is similar to that found in the electronically and sterically equivalent alkyl derivative $Mo_2(O_2CMe)_2(CH_2SiMe_3)_2(PMe_3)_2$.[7] The most notable difference between the two structures occurs in the Mo–P distances: 2.547 (1) Å in the alkyl and 2.487 (1) Å in the siloxide. This difference is most reasonably ascribed to the low position of siloxide ligands relative to alkyls on the trans-influence series, which agrees with the order deduced in square-planar Pt(II) chemistry.[8]

In our initial attempts to study the phosphine substitution kinetics, we found that the exchange rates in the series $Mo_2(O_2CCMe_3)_2X_2(PEt_3)_2$ where X is alkyl, halide, amide, or siloxide were too rapid to be followed conveniently by $^{31}P\{^1H\}$ NMR spectroscopy.[9] Since kinetics studies in the $Mo_2Me_4(PR_3)_4$ system showed that smaller phosphines exhibit slower rates,[1] we prepared the series $Mo_2(O_2CCMe_3)_2X_2(PMe_2Et)_2$.[10] These compounds

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(5) Anal. Calcd: C, 30.0; H, 6.61. Found: C, 30.3; H, 6.66. Mp 157–158 °C; ^1H NMR (PhH-d_6, 25 °C) δ 2.63 (O_2CMe, s), 1.28 (PMe_3, $AA'X_9X'_9$, $^2J_{AX} + {}^5J_{A'X} = 9$ Hz), 0.20 ($OSiMe_3$, s); $^{13}C\{^1H\}$ NMR (PhH-d_6, 20 °C) δ 183.4 (O_2CMe, s), 23.2 (O_2CMe, s), 11.9 (PMe_3, ABX, $^1J_{AX} + {}^4J_{BX} = 26$ Hz), 4.1 ($OSiMe_3$, s); $^{31}P\{^1H\}$ NMR (PhH-d_6, 25 °C) δ 5.0, s.

(6) Single crystals of $Mo_2(O_2CMe)_2(OSiMe_3)_2(PMe_3)_2$ are triclinic, space group $P\bar{1}$, with $a = 11.465$ (2) Å $b = 11.544$ (1) Å $c = 13.695$ (2) Å, $\alpha = 70.54$ (1)°, $\beta = 64.12$ (1)°, $\gamma = 77.54$ (1)°, $V = 1532.4$ (3) Å^3; $Z = 2$. X-ray diffraction data were collected for 4015 independent reflections having $2\theta < 45°$ on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo Kα radiation and θ–2 θ scans. The structure was solved by the heavy-atom method. The final residuals for 254 variables refined against the 3564 data for which $F^2 > 3\sigma(F^2)$ were $R_F = 2.29\%$, $R_{wF} = 4.22\%$, and GOF = 2.23. In the last cycle, hydrogen atom positions were predicted and included in the structure factor calculations, but not refined.

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(8) *cis*-$Pt(OSiMe_3)_2(PMe_3)_2$ has $^1J_{Pt-P} = 3400$ Hz,[8a] while *cis*-$Pt(CH_2SiMe_3)_2(PMe_2Ph)_2$ has $^1J_{Pt-P} = 1999$ Hz,[8b] showing that $CH_2SiMe_3 > OSiMe_3$ on a trans series. (a) Schmidbaur, H.; Adlkofer, J. *Chem. Ber.* **1974**, *107*, 3680–3683. (b) Cardin, C. J.; Cardin, D. J.; Lappert, M. F.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1978**, 46–50. For general references on trans-influence series, see: Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335–422. Manojlovic-Muir, L.; Muir, K. W. *Inorg. Chim. Acta* **1974**, *10*, 47–49.

(9) The pivalate derivatives were used since they are more soluble in toluene at low temperature than their corresponding acetate analogues. Rate studies have shown that phosphine-exchange rates for the neopentyl derivatives $Mo_2(O_2CR)_2(CH_2CMe_3)_2(PMe_2Et)_2$ are independent of the carboxylate group (R = Me, CF_3, or CMe_3).

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undergo phosphine exchange with PMe_3 at rates that can be followed satisfactorily by $^{31}P\{^1H\}$ NMR spectroscopy.

Reaction with excess PMe_3 at low temperature in toluene forms the mixed-phosphine intermediates $Mo_2(O_2CCMe_3)_2X_2(PMe_2Et)(PMe_3)$ before the second exchange occurs to give the fully substituted bis-PMe_3 product. The $^{31}P\{^1H\}$ spectra of the mixed-phosphine intermediates are characteristic of AB spin systems, with each phosphine resonance being split into a doublet of separation $^3J_{PP}$. The magnitude of the coupling constant reflects the trans-influence ability of the X group as shown in Table I. As X becomes a poorer trans-influence ligand, the molybdenum-phosphorus bond becomes stronger (as shown by the Mo–P bond lengths discussed above), and the phosphorus–phosphorus coupling constants increase. Thus, the trans-influence series alkyl > halide > amide > siloxide may be deduced for binuclear complexes of stereochemistry II.

Having established that the exchange process is stepwise, as was found in molecules of stereochemistry I,[1] we studied the kinetics of substitution for the first phosphine ligand as a function of the X group. We can minimize complications due to steric effects by choosing the two anionic groups at the extremes of Table I (CH_2CMe_3 and $OSiMe_3$), as they are very similar in size. Thus, the alkyl derivative $Mo_2(O_2CCMe_3)_2(CH_2CMe_3)_2(PMe_2Et)_2$ reacts with an excess of PMe_3 at −30 °C in toluene following first-order kinetics with $k_{obsd} = (1.00 \pm 0.05) \times 10^{-4}\ s^{-1}$. No rate dependence on $[PMe_3]$ was observed over a range of 10–20 molar equiv/binuclear unit. An Arrhenius plot over three temperatures gave $\Delta H^{\ddagger} = 22.2$ kcal mol^{-1} and $\Delta S^{\ddagger} = 15$ eu. The positive entropy of activation implies a *dissociative* mechanism for molecules of structure II, as observed previously for $Mo_2Me_4(PR_3)_4$.[1] The siloxide derivative $Mo_2(O_2CCMe_3)_2(OSiMe_3)_2(PMe_2Et)_2$ reacts in a similar manner with PMe_3, except that a higher temperature is necessary to achieve a similar rate. At 0 °C, $k_{obsd} = (1.97 \pm 0.05) \times 10^{-4}\ s^{-1}$, and Arrhenius parameters of $\Delta H^{\ddagger} = 24.7$ kcal mol^{-1} and $\Delta S^{\ddagger} = 15$ eu can be obtained.

Extrapolating the observed rate data to similar temperatures, we find that the phosphine dissociation rates are 10^2 times faster in the alkyl derivative than in the siloxide. This rate difference is most reasonably ascribed to a kinetic trans effect, where $CH_2SiMe_3 > OSiMe_3$ in a trans series. Hence the rate data, in conjunction with the structural and spectroscopic results, strongly indicate that both a trans influence and a trans effect are operating in these binuclear, quadruply bonded compounds.

Acknowledgment. We thank the NSF for departmental grants used to purchase the NMR spectrometers and X-ray diffractometer used in this work and Chevron (G.S.G.) and the UCB equal opportunity fund (V.V.M.) for fellowships. We also thank Dr. F. J. Hollander, staff crystallographer at the UCB X-ray crystallographic facility (CHEXRAY), for performing the X-ray study.

Registry No. $Mo_2(O_2CCMe_3)_2(OSiMe_3)_2(PMe_3)_2$, 80925-85-5; $Mo_2(O_2CCMe_3)_2(CH_2CMe_3)_2(PMe_2Et)(PMe_3)$, 80925-86-6; $Mo_2(O_2CCMe_3)_2(CH_2SiMe_3)(PMe_2Et)(PMe_3)$, 80925-87-7; $Mo_2(O_2CCMe_3)_2(Me)_2(PMe_2Et)(PMe_3)$, 80925-88-8; $Mo_2(O_2CCMe_3)_2I_2(PMe_2Et)(PMe_3)$, 80925-89-9; $Mo_2(O_2CCMe_3)_2Cl_2(PMe_2Et)(PMe_3)$, 80925-90-2; $Mo_2(O_2CCMe_3)_2Br_2(PMe_2Et)(PMe_3)$, 80925-91-3; $Mo_2(O_2CCMe_3)_2(N(SiMe_2H)_2)_2(PMe_2Et)(PMe_3)$, 80925-92-4; $Mo_2(O_2CCMe_3)_2(OSiMe_3)_2(PMe_2Et)(PMe_3)$, 80925-93-5; $Mo_2(O_2CCMe_3)_2(CH_2CMe_3)_2(PMe_2Et)_2$, 80939-27-1; $Mo_2(O_2CCMe_3)_2(OSiMe_3)_2(PMe_2Et)_2$, 80925-94-6; $Mo_2(O_2CCMe_3)_4$, 55946-68-4; PMe_3, 594-09-2.

Supplementary Material Available: A listing of positional and thermal parameters and their estimated standard deviations (1 page). Ordering information is given on any current masthead page.

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(10) The alkyl derivatives were prepared as in ref 2, the amide as in ref 3, and the halides as in ref 4. All compounds gave satisfactory elemental analysis, and NMR spectral properties (^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$) show them to be of the structural type II.

Characterization of Several Novel Iron Nitrosyl Porphyrins

L. W. Olson,† D. Schaeper, D. Lançon, and K. M. Kadish*

Department of Chemistry, University of Houston
Houston, Texas 77004

Received November 16, 1981

Considerable attention has been given to the chemistry of synthetic transition-metal metalloporphyrins complexed by diatomic molecules.[1,2] Because of their relevance to biological systems, the reactions of Fe(II) porphyrin complexes with diatomic molecules such as O_2, CO, CS, and NO have been of special interest.

It has been reported[3] that the five-coordinate complexes of PorFeNO (where Por = TPP^{2-} (tetraphenylporphyrin) or OEP^{2-} (octaethylporphyrin)) can be reversibly oxidized by cyclic voltammetry at a Pt electrode to yield $[PorFeNO]^+$. In this communication we report the isolation and characterization of a novel bis(nitrosyl) complex of Fe(III), $[PorFe(NO)_2]^+$. We also report the reversible electrochemical reduction of PorFeNO to yield $[PorFeNO]^-$.

(TPP)FeNO and (OEP)FeNO are low-spin, five-coordinate complexes of Fe(II).[2-4] Cyclic voltammetry of these complexes at a Pt electrode in CH_2Cl_2, 0.1 M TBAP (tetra-*n*-butylammonium perchlorate), reveals that each neutral species undergoes a reversible one-electron oxidation and a reversible one-electron reduction during the time scale of the experiment. This is shown in Figure 1, and the potentials of the reactions are listed in Table I. Also listed in this table are potentials for several representative five- and six-coordinate complexes of (TPP)Fe and (OEP)Fe in both CH_2Cl_2 and pyridine. As seen from this table, the potentials for oxidation of PorFeNO are extremely positive and are, in fact, the most positive ever reported for the reaction Fe(II) $\rightleftarrows$ Fe(III). This substantial stability of the ferrous form is reflected in the relative inertness of PorFeNO to air oxidation and to displacement by other ligands.[4] The differences between the OEP and TPP complexes reflect the greater basicity of the OEP^{2-} ring and are consistent with differences observed for other complexes of the two porphyrins.[5]

Oxidation of PorFeNO greatly increases the lability of the nitrosyl ligand. Attempts to isolate $[PorFeNO]^+$ by controlled-potential coulometry in CH_2Cl_2 at 1.0 V vs. SCE, 0.1 M TBAP, produced only $PorFeClO_4$ as determined by electronic spectra.[6] However, electrolysis under an atmosphere of nitric oxide rather than nitrogen produced a new compound whose electronic spectrum is shown in Figure 2. Two Soret bands of significantly lowered intensity are observed for both OEP and TPP derivatives. Purging the solution with an inert gas results in appearance of the perchlorate spectrum. Conversely, exposure of solutions of $PorFeClO_4$ to nitric oxide regenerates the spectrum in Figure 2.

Crystalline solids may be obtained from CH_2Cl_2/hexane solutions, but decomposition occurs unless they are stored under nitric oxide. Two N–O stretching frequencies in the infrared spectrum at 1940 and 1860 cm^{-1} (TPP derivative) provide evidence that this new species is the bis(nitrosyl) complex $[PorFe(NO)_2]^+ClO_4^-$. The perchlorate region is typical of ionic rather than coordinated ClO_4^-.[6] Conductivity studies in CH_2Cl_2 under NO show a molar conductivity of 40.8 Ω^{-1} cm^2 mol^{-1}, consistent with a 1:1 electrolyte such as TBAP and much larger than a

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† On leave of absence from Grand Canyon College, Phoenix, AZ 85017.

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