Table I. Competitive Epoxidation of α-Methylstyrene and Norbornylene with Peracids Catalyzed by Iron(III)

run	catalyst	oxidant	solvent	temp, °C	% yield	selectivity[a] (norbornylene oxide (endo %)/ α-methylstyrene oxide)[b]	ratio of selectivity in toluene/CH_2Cl_2
1	none	*m*-CPBA	CH_2Cl_2	*c*	76	100 (0):30	1.4
2	none	*m*-CPBA	toluene	*c*	62	100 (0):42	
3	FeTMP(Cl)	*m*-CPBA	CH_2Cl_2	−78	63	100 (4):9	8.2
4	FeTMP(OH)	*m*-CPBA	CH_2Cl_2	−78	65	100 (6):10	7.4
5	FeTMP(OH)	*m*-CPBA	toluene	−78	65	100 (2):74	
6	FeTDMPP(Cl)	*m*-CPBA	CH_2Cl_2	−78	98	100 (24):29	5.1
7	FeTDMPP(OH)	*m*-CPBA	toluene	−78	47	100 (<1):148	
8	FeTDCPP(Cl)	*m*-CPBA	CH_2Cl_2	−78	63	100 (6):59	1.4
9	FeTDCPP(OH)	*m*-CPBA	CH_2Cl_2	−78	72	100 (10):57	1.4
10	FeTDCPP(OH)	*m*-CPBA	toluene	−78	44	100 (1):82	
11	FeTPFPP(Cl)	*m*-CPBA	CH_2Cl_2	−78	98	100 (2):73	1.3
12	FeTPFPP(Cl)	*m*-CPBA	toluene	−78	42	100 (5):98	
13	none	*o*-CPBA	CH_2Cl_2	*c*	93	100 (0):22	1.8
14	none	*o*-CPBA	toluene	*c*	96	100 (0):39	
15	FeTMP(Cl)	*o*-CPBA	CH_2Cl_2	−78	53	100 (2):9	10.1
16	FeTMP(OH)	*o*-CPBA	toluene	−78	51	100 (<1):91	
17	FeTDMPP(Cl)	*o*-CPBA	CH_2Cl_2	−78	47	100 (22):30	
18	FeTDCPP(Cl)	*o*-CPBA	CH_2Cl_2	−78	96	100 (4):73	1.5
19	FeTDCPP(OH)	*o*-CPBA	toluene	−78	52	100 (3):113	

[a] Determined by GLC. [b] See ref 6. [c] Room temperature.

tributed to the alternation of the reactive species of the iron porphyrin.

Halogenated iron porphyrins such as Fe^{III}TDCPP and Fe^{III}TPFPP[2] are known as good catalysts for many oxidations;[1j,o,p,9] however, the reaction of *m*-CPBA with these iron porphyrins in CH_2Cl_2 at −78 °C failed to form the green intermediates even without olefins.[10] Thus, the reaction of Fe^{III}TDCPP(OH) and *m*-CPBA in CH_2Cl_2 at −78 °C was examined by UV-vis spectroscopy. As shown in Figure 1A, introduction of *m*-CPBA gave a new species (A), which was stable under the condition. This new species is determined to be Fe^{III}TDCPP(*m*-CPBA) (**3b**) since **3b** oxidized 2 equiv of tetra-*n*-butyl ammonium iodide. Replacement of the solvent with toluene yielded the *N*-oxide of Fe^{III}TDCPP via a transient formation of (**3b**) under the same condition. Interestingly, while the oxidations of a mixture of norbornylene and α-methylstyrene were catalyzed by these halogenated iron porphyrins in CH_2Cl_2 and toluene at −78 °C, the shape selectivities were found to be similar in both solvents (Table I, runs 8–12). The ratios of selectivities of α-methylstyrene over norbornylene in toluene to CH_2Cl_2 were calculated to be 1.3–1.5. In addition, the epoxidation of the olefins by *m*-CPBA also showed a small solvent effect on the shape selectivity (ratio of selectivities was 1.4).

Comparable production of norbornylene oxide and α-methylstyrene oxide is rather indicative of the active species to be different from the oxo intermediate (**1**) even in CH_2Cl_2. As shown in Scheme I and Figure 1, a peracid–iron porphyrin complex (**3**) is the common intermediate certainly observed in both solvent systems. Further, peracid–manganese porphyrin complexes are known to oxidize olefins.[11] All these results suggest that the active species in the epoxidation is **3** when the formation of **1** is less favorable process. Recently, a very similar metal–oxidant adduct participation in the olefin epoxidations has been suggested.[12] If the adduct is responsible for the epoxidations, the shape selectivity would be dependent on the structure of peracids employed, while the selectivity must remain unchanged when **1** is the active species. Thus, the iron porphyrin catalyzed competitive epoxidations were carried out with *o*-CPBA.[2] As shown in Table I (runs 15–19), only the shape selectivity of norbornylene and α-methylstyrene catalyzed by FeTMP and FeTDMPP in CH_2Cl_2 was not affected by the structure of the peracid.

In conclusion, we have shown that there are two types of active species responsible for the epoxidation when a peracid–iron(III) porphyrin system was employed. Oxo–ferryl porphyrin cation radicals (**1**) preferably oxidized *cis*-olefin. A peracid–iron(III) porphyrin complex (**3**) was proposed to be an alternative reactive species in the oxidation where comparable epoxide formation of norbornylene and α-methylstyrene was observed.

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(9) (a) Traylor, T. G.; Nakano, T.; Dunlap, B. E.; Traylor, P. S.; Dolphin, D. *J. Am. Chem. Soc.* **1986**, *108*, 2782–2784. (b) Battioni, P.; Renaud, J. P.; Bartoli, J. F.; Reina-Artiles, M.; Fort, M.; Mansuy, D. *Ibid.* **1988**, *110*, 8462–8470. (c) De Poorter, B.; Ricci, M.; Bortolini, O.; Meunier, B. *J. Mol. Cat.* **1985**, *31*, 221–224. (d) Tsuchiya, S.; Senô, M. *Chem. Lett.* **1989**, 263–266.

(10) While we failed to prepare higher-valent iron porphyrin derivatives of Fe^{III}TDCPP and Fe^{III}TPFPP under the conditions, Gold et al. reported the formation of $O{=}Fe^{IV}$TDCPP in THF. Further, Sawyer et al. prepared $O{=}Fe^{IV}TDCPP^{\bullet +}$ in acetonitrile. Gold, A.; Jayaraj, K.; Doppelt, P.; Weiss, R.; Chottard, G.; Bill, E.; Ding, X.; Trautwein, A. X. *J. Am. Chem. Soc.* **1988**, *110*, 5756–5761; Sugimoto, H.; Tung, H.-C.; Sawyer, D. T. *Ibid.* **1988**, *110*, 2465–2470.

(11) Groves, J. T.; Watanabe, Y.; McMurry, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 4489–4490.

(12) Yang, Y.; Diederich, F.; Valentine, J. S. *J. Am. Chem. Soc.* **1990**, *112*, 7826–7830.

Mononuclear *cis*-Carbonyloxotungsten(IV) Complexes of Hydrotris(3,5-dimethyl-1-pyrazolyl)borate

Mononuclear complexes containing the cylindrically symmetrical but electronically disparate carbonyl π-acid and oxo π-base ligands are extremely rare. Prior to 1986, complexes of this type had been identified only in matrix-isolation and gas-phase experiments.[1-5] In 1986, Mayer and co-workers[6] reported the first

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(1) Poliakoff, M.; Smith, K. P.; Turner, J. J.; Wilkinson, A. J. *J. Chem. Soc., Dalton Trans.* **1982**, 651–657.

(2) Lane, K.; Sallans, L.; Squires, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 2719–2721.

(3) Crayston, J. A.; Almond, M. J.; Downs, A. J.; Poliakoff, M.; Turner, J. J. *Inorg. Chem.* **1984**, *23*, 3051–3056.

(4) Almond, M. J.; Downs, A. J.; Perutz, R. N. *Inorg. Chem.* **1985**, *24*, 275–281.

0020-1669/91/1330-2582$02.50/0

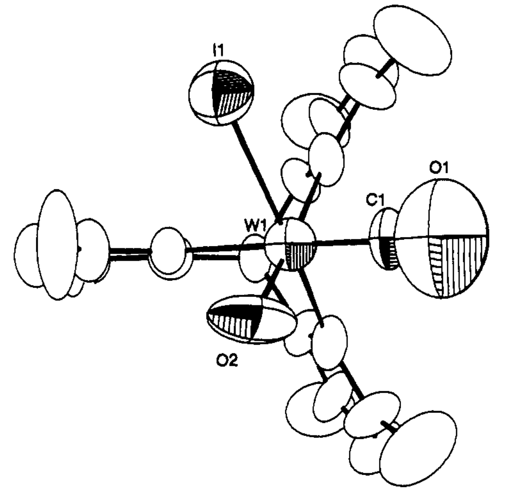

Figure 1. Molecular structure of **1** showing the atom-labeling scheme.

isolation of a stable mononuclear *cis*-carbonyloxotungsten(IV) complex, $WOCl_2(CO)(PMePh_2)_2$, formed either by reaction of $WOCl_2(PMePh_2)_3$ with CO[6] or by oxidative addition of CO_2 to $WCl_2(PMePh_2)_4$.[7] The synthesis and properties of this and related π-acceptor and π-donor ligand complexes have been described in detail.[8] The recent characterization of a dinuclear carbonyloxotungsten complex, $\{HB(Me_2pz)_3\}_2W^{IV}O(CO)(\mu\text{-}O)W^{VI}O_2\{HB(Me_2pz)_3\}$ [$HB(Me_2pz)_3^-$ = hydrotris(3,5-dimethyl-1-pyrazolyl)borate anion],[9] and an awareness of the ability of the $HB(Me_2pz)_3^-$ ligand to stabilize otherwise reactive ligands, such as terminal thio[10,11] and nitrido[12] ligands, in mononuclear complexes led us to explore the synthesis of mononuclear carbonyl oxo complexes with $HB(Me_2pz)_3^-$ in the coordination sphere. We now report the high-yield synthesis of $\{HB(Me_2pz)_3\}WO(CO)X$ complexes, which are formed by direct oxidation of a tungsten(II) carbonyl reagent with molecular oxygen. Retention of even one carbonyl ligand in the oxidized products is a surprising aspect of these syntheses.

Oxidation of $NEt_4[\{HB(Me_2pz)_3\}W(CO)_3]$ by iodine or bromine in dichloromethane or acetonitrile affords 80% yields of brown $\{HB(Me_2pz)_3\}W(CO)_3X$ ($X = I^-$, $\nu(CO)$ = 2012, 1915, 1872 cm^{-1}; $X = Br^-$, $\nu(CO)$ = 2026, 1916 (br) cm^{-1}) (eq 1).[13] Further

$$NEt_4[\{HB(Me_2pz)_3\}W(CO)_3] + X_2 \rightarrow \{HB(Me_2pz)_3\}W(CO)_3X + NEt_4X \quad (1)$$

$$\{HB(Me_2pz)_3\}W(CO)_3X + O_2 \rightarrow \{HB(Me_2pz)_3\}WO(CO)X + CO_2 + CO \quad (2)$$

oxidation of $\{HB(Me_2pz)_3\}W(CO)_3X$ by molecular oxygen in refluxing toluene ($X = I^-$) or hot acetonitrile ($X = Br^-$) yields purple ($X = I^-$) or pink-purple ($X = Br^-$) $\{HB(Me_2pz)_3\}WO(CO)X$ (eq 2), which may be isolated by crystallization following volume reduction/cooling of the reaction mixture.[14,15] The production of carbon dioxide as an additional reaction product was established by passing the gaseous products through aqueous calcium hydroxide solution. Salient spectral features associated with the carbonyl oxo products include strong infrared absorptions at about 1975 and 953 cm^{-1} for $\nu(CO)$ and $\nu(W{=}O)$, respectively, the ^1H NMR inequivalence of the three pyrazole rings of $HB(Me_2pz)_3^-$ (indicative of molecular C_1 symmetry in these chiral molecules), and an unusually low-field ^{13}C signal near 280 ppm assigned to the carbonyl carbon. The one-bond coupling between the carbonyl carbon and tungsten (^{183}W, $I = {}^1/_2$, 14%) of about 190 Hz is also unusually large.

The solid-state structure[16] of $\{HB(Me_2pz)_3\}WO(CO)I$ (Figure 1) confirms the presence of mononuclear distorted octahedral molecules, but disorder between the oxo and iodo ligands severely limits discussion of the structure. Bond distances within the molecule include W(1)–O(2) = 1.80 (3) Å, W(1)–C(1) = 1.75 (3) Å, W(1)–I(1) = 2.816 (3) Å, W(1)–N(11) and W(1)–N(11a) = 2.20 (1) Å, and W(1)–N(21) = 2.23 (2) Å. While the W–N distances would be expected to reflect the relative trans influences of the oxo, carbonyl, and iodo ligands, this effect is masked by the disorder problem. In the related dinuclear carbonyloxotungsten complex described by Young et al.,[9] a $[\{HB(Me_2pz)_3\}WO_2(\mu\text{-}O)]^-$ unit, rather than an iodo ligand, occupies the sixth coordination site of a $[\{HB(Me_2pz)_3\}WO(CO)]^+$ fragment. Both complexes exhibit similar *cis*-oxocarbonyl geometries, but disorder in both structures precludes an informative presentation of bond distances. Although the X-ray structure of $\{HB(Me_2pz)_3\}WO(CO)I$ has confirmed the mononuclearity of the title compounds, a detailed structural description of this type of compound awaits the synthesis of an ordered crystalline derivative.

The electronic preference for a *cis*-oxocarbonyl arrangement to optimize π-donor and π-acceptor properties has been presented

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(5) Almond, M. J.; Crayston, J. A.; Downs, A. J.; Poliakoff, M.; Turner, J. J. *Inorg. Chem.* **1986**, *25*, 19–25.

(6) Su, F.-M.; Cooper, C.; Geib, S. J.; Rheingold, A. L.; Mayer, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 3545–3547.

(7) Bryan, J. C.; Geib, S. J.; Rheingold, A. L.; Mayer, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 2826–2828.

(8) Su, F.-M.; Bryan, J. C.; Jang, S.; Mayer, J. M. *Polyhedron* **1989**, *8*, 1261–1277.

(9) Young, C. G.; Gable, R. W.; Mackay, M. F. *Inorg. Chem.* **1990**, *29*, 1777–1779.

(10) Young, C. G.; Enemark, J. H.; Collison, D.; Mabbs, F. E. *Inorg. Chem.* **1987**, *26*, 2925–2927.

(11) Young, C. G.; Roberts, S. A.; Ortega, R. B.; Enemark, J. H. *J. Am. Chem. Soc.* **1987**, *109*, 2938–2946.

(12) Young, C. G.; Janos, F.; Bruck, M. A.; Wexler, P. A.; Enemark, J. H. *Aust. J. Chem.* **1990**, *43*, 1347–1355.

(13) Preparation of $\{HB(Me_2pz)_3\}W(CO)_3X$: A suspension of $NEt_4[\{HB(Me_2pz)_3\}W(CO)_3]$ in acetonitrile or dichloromethane was treated with 1 equiv of halogen and stirred at room temperature. Passage of the reduced reaction mixture through an alumina column using toluene as eluant results in a brown fraction, which when evaporated yields $\{HB(Me_2pz)_3\}W(CO)_3X$. Detailed syntheses of these compounds will be reported elsewhere.

(14) Synthesis of $\{HB(Me_2pz)_3\}WO(CO)I$ (**1**): A solution of $\{HB(Me_2pz)_3W(CO)_3I$ (2.0 g, 2.89 mmol) in toluene (100 mL) was heated to reflux while a slow flow of air was maintained through the solution. After 4 h, the initial red solution had changed to purple and a solution infrared spectrum revealed a single strong band at 1980 cm^{-1}. The volume of the solution was reduced to 30 mL, and the mixture was chromatographed on alumina using toluene as eluant. The purple fraction was collected, reduced in volume to ca. 10 mL and placed at −40 °C overnight. The crystalline product was isolated by filtration and vacuum dried (yield 1.5 g, 80%). Anal. Calcd for $C_{23}H_{30}BIN_6O_2W$ ($1\cdot C_6H_5Me$): C, 37.12; H, 4.03; N, 11.30; I, 17.07. Found: C, 36.64; H, 3.96; N, 11.39; I, 17.74. (Partial loss of toluene evident from analysis.) IR (KBr, cm^{-1}): $\nu(BH)$ 2557 m, $\nu(CO)$ 1975 s, $\nu(CN)$ 1543 m, $\nu(W{=}O)$ 953 m. ^1H NMR (CD_2Cl_2): δ (vs $SiMe_4$) 2.29, 2.38, 2.51, 2.57, 2.58, and 2.91 (each s, 3 H, Me of $HB(Me_2pz)_3^-$), 5.70, 6.08, and 6.26 (each s, 1 H, CH of $HB(Me_2pz)_3^-$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ (vs CD_2Cl_2) 12.5, 12.7, 12.9, 16.5, 17.3, and 18.2 (s, 6 CH_3), 107.8, 107.9, and 109.1 (s, 3 *C*H), 146.1, 146.9, and 147.9 (s, 3 *C*Me), 153.6, 154.0, and 154.4 (s, 3 *C*Me), 278.7 ($^1J_{WC}$ = 189 Hz, *C*O).

(15) Synthesis of $\{HB(Me_2pz)_3\}WO(CO)Br$ (**2**): A solution of $\{HB(Me_2pz)_3W(CO)_3Br$ (2.0 g, 3.1 mmol) in acetonitrile (20 mL) was heated at 80 °C for 2 h. The mixture was then cooled overnight. The product was isolated by filtration and was washed with a small amount of cold acetonitrile. Yield: 1.1 g, 60%. To date we have not been able to prevent a small degree of further oxidation to $\{HB(Me_2pz)_3\}WO_2Br$ nor have we been able to separate the two compounds. Hence a microanalysis has not been obtained. IR (KBr, cm^{-1}): $\nu(BH)$ 2555 (m), $\nu(CO)$ 1977 (s), $\nu(CN)$ 1523 (m), $\nu(W{=}O)$ 957 (m). ^1H NMR (CD_2Cl_2): δ (vs $SiMe_4$) 2.29, 2.36, 2.53, 2.56, 2.58, and 2.87 (each s, 3 H, Me of $HB(Me_2pz)_3^-$), 5.71, 6.09, and 6.24 (each s, 1 H, CH of $HB(Me_2pz)_3^-$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ (vs CD_2Cl_2): 12.4, 12.5, 12.7, 15.7, 16.2, and 16.4 (s, 6 CH_3), 107.5, 107.6, and 108.8 (s, 3 *C*H), 145.8, 146.8, and 147.6 (s, 3 *C*Me), 153.1, 153.6, and 154.0 (s, 3 *C*Me), 283.2 ($^1J_{WC}$ = 194 Hz, *C*O).

(16) Crystal data for **1**, $\{HB(Me_2pz)_3\}WO(CO)I$: space group $P2_1/m$, a = 8.068 (5) Å, b = 18.744 (4) Å, c = 9.134 (6) Å, β = 98.49 (6)°, Z = 2, d_{calc} = 1.760 g·cm^{-3}, μ(Mo Kα) = 54.5 cm^{-1}. The 2488 reflections were measured on a Nonius CAD-4 diffractometer using the θ–2θ scan mode; 1464 were above the $2.5\sigma(I)$ level and were treated as observed. The structure was solved by Patterson and Fourier methods. Anisotropic refinement of non-hydrogen atoms converged to $R = 0.060$ (R_w = 0.077). The structure is disorderd with a mirror plane passing through the molecule. This results in superposition of the W—I and W=O bonds. Also, O(2) has an extremely large thermal parameter, and the C(2)–O(2) bond length is short; this is presumably a figment of the disorder.

previously.[8,17] The cis disposition of these ligands allows π-back-bonding between the filled d_{xy} (taking z as the direction along W=O) and the π^* CO orbitals. The mutual cis arrangement of the oxo, carbonyl, and halide ligands is also dictated by the facial coordination mode of the $HB(Me_2pz)_3^-$ ligand in these complexes. We believe the steric protection offered to the WO(CO)X fragment by the $HB(Me_2pz)_3^-$ ligand enhances the kinetic stability of the $\{HB(Me_2pz)_3\}WO(CO)X$ complexes. We note that further oxidation of the complexes to the more thermodynamically stable *cis*-dioxotungsten(VI) complexes $\{HB(Me_2pz)_3\}WO_2X$ does take place, and indeed, the susceptibility of the bromo complex to this reaction has made it difficult to isolate pure $\{HB(Me_2pz)_3\}WO(CO)Br$. The mechanism of the reaction, which appears to proceed via an isolable as yet uncharacterized dicarbonyl intermediate, is of great interest and is under further study.

Preliminary studies of the reactivity of **1** have revealed that the phenylnitrene complex $\{HB(Me_2pz)_3\}W(NPh)(CO)I$[18] is formed upon reaction with aniline (eq 3). The CO frequency of 1930 cm^{-1} indicates that greater electron density is available for back-bonding in the nitrene complex than in the oxo analogue (ν_{CO} = 1975 cm^{-1}) as was found by Mayer and co-workers.[8] NMR reveals the carbonyl carbon at 278.7 ppm with $^1J_{WC}$ = 178 Hz while the ipso carbon of the nitrene phenyl group displays two-bond coupling to tungsten ($^2J_{WC}$ = 35 Hz). Similar two-bond coupling has been reported for related cationic nitrenes with phenyl and *tert*-butyl substituents.[19]

$$\{HB(Me_2pz)_3\}WO(CO)I + PhNH_2 \rightarrow \{HB(Me_2pz)_3\}W(NPh)(CO)I \quad (3)$$

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Supplementary Material Available: Tables giving a summary of the crystal data and details of the X-ray data collection, atomic fractional coordinates, thermal parameters, and complete interatomic distances and angles and a drawing of **1** showing the complete atomic labeling (7 pages); a list of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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(17) Brower, D. C.; Templeton, J. L.; Mingos, D. M. P. *J. Am. Chem. Soc.* **1987**, *109*, 5203.

(18) Synthesis of $\{HB(Me_2pz)_3\}W(NPh)(CO)I$: A solution of $\{HB(Me_2pz)_3\}W(CO)(O)I$ (1.00 g, 1.53 mmol) in aniline (50 mL) was heated to 80 °C for 4 h, and the color changed from red-brown to brown. The solvent was removed under reduced pressure. The residue was recrystallized from CH_2Cl_2/MeOH three times to yield dark brown crystals (0.57 g, 46%). IR (KBr, cm^{-1}): ν(CO) 1930. ^{1}H NMR (CD_2Cl_2): δ 7.40 (m, 3 H, C_6H_5), 7.25 (m, 2 H, C_6H_5), 6.12, 6.01, and 5.80 [1:1:1, 3 H, CH of $HB(Me_2pz)_3$], 2.56, 2.55, 2.53, 2.50, 2.36, and 2.29 [3:3:3:3:3:3, 18 H, CH_3 of $HB(Me_2pz)_3$]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 278.7 ($^1J_{WC}$ = 178 Hz, CO), 158.1 ($2J_{WC}$ = 35 Hz, C ipso), 154.3, 154.2, 153.5, 146.4, 146.3, and 146.0 (CCH_3), 129.7, 126.6, and 125.1 (C_6H_5), 108.4, 107.9, and 107.3 (CH_3), 18.0, 17.5, 16.3, 13.0, 12.72, and 12.68 (CCH_3). Anal. Calcd for $WBN_7C_{22}H_{27}OI \cdot CH_2Cl_2$: C, 34.02; H, 3.60. Found. C, 34.27; H, 3.76.

(19) Luan, L.; White, P. S.; Brookhart, M.; Templeton, J. L. *J. Am. Chem. Soc.* **1990**, *112*, 8190.

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Linear Trimeric and Monomeric Octahedral Vanadium(II) Diphenylacetate Complexes

The ability of carboxylate anions to work as bridging three-center chelating ligands is an attractive feature of this class of molecules widely employed for the assemblage of di-[1] and polymetallic units.[2] The most useful characteristics of carboxylate anions as ligands can be summarized in the ability (i) to easily form dimers via bridging interactions of the two oxygen donor atoms, each binding one of the two metal centers,[1] (ii) to accommodate an enormous range of M–M distances (from very short[3] to considerably long nonbonding distances),[4] and (iii) to establish efficient magnetic couplings between two metal centers.[5] Thus, structural investigations on transition-metal carboxylates may be helpful for understanding the nature of the M–M interaction.

Among low-valent early transition metals, vanadium(II) carboxylates are especially interesting because of some attractive performances expected or reported for these species, including dinitrogen fixation[6] and formation of short V–V triple bonds.[7] Early theoretical work has predicted the stability of dimeric vanadium(II) carboxylate with a V–V bonding distance of ca. 2.2 Å.[7c] Although initial attempts to prepare vanadium(II) carboxylates have been hampered by the apparent tendency of vanadium(II) to abstract oxygen from the $-COO^-$ group to form a mixed-valence $[V_3O]$ core,[8] an encouraging result describing the preparation of cationic $[V_2(CF_3COO)_2Cl(THF)_6]^+$ has been recently reported.[9] However, no neutral vanadium(II) carboxylates have been reported to date. In this paper, we wish to report the preparation and characterization of the first linear trimeric vanadium(II) carboxylates, together with their facile cleavage.

In a standard experiment, a solution of $VCl_2(TMEDA)_2$[10,11]

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(1) For some selected examples of transition metals, see: (a) Gilson, T. R.; Thom-Postlethwaite, I. M.; Webster, M. *J. Chem. Soc., Dalton Trans.* **1986**, 895. (b) Head, H. L.; Halley, C. E. *J. Inorg. Nucl. Chem.* **1964**, *26*, 525. (c) Guseinova, M. K.; Antsyshkina, A. S.; Parai-Koshits, M. A. *J. Struct. Chem.* (*Engl. Transl.*) **1968**, *9*, 926. (d) Jelenic, I.; Grdenic, G.; Bezjack, A. *Acta Cryst.* **1964**, *17*, 758. (e) Hessel, L. W.; Romers, C. *Recl. Trav. Chim. Pays-Bas* **1969**, *88*, 545. (f) Blake, A. B.; Fraser, L. R. *J. Chem. Soc., Dalton Trans.* **1975**, 193. (g) Catterick, J.; Thornton, P. *J. Chem. Soc., Dalton Trans.* **1977**, 1420. (h) Rakitin, Y. V.; Volkov, V. V.; Kalinnikov, V. T. *Koord. Khim.* **1980**, *6*, 451. (i) Bennet, M. J.; Caulton, K. G.; Cotton, F. A. *Inorg. Chem.* **1969**, *8*, 1. (j) Bino, A.; Cotton, F. A.; Felthouse, T. R. *Inorg. Chem.* **1979**, *18*, 2599. (k) Buckingam, D. A.; Clark, C. R. In *Comprehensive Coordination Chemistry*, Wilkinson, G. Ed.; Pergamon Press: Oxford, England, 1986, and references cited herein. (l) Cotton, F. A.; deBoer, B. G.; LaPrade, M. D.; Pipal, J. R.; Veko, D. A. *J. Am. Chem. Soc.* **1970**, *92*, 2926. (m) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; J. Wiley & Sons: New York, 1982, and references cited therein.

(2) Taft, K. L.; Lippard, S. J. *J. Am. Chem. Soc.* **1990**, *112*, 9629.

(3) (a) Cotton, F. A.; Walton, R. A. Metal-Metal Multiple Bonds in Dinuclear Cluster. *Struct Bonding* (*Berlin*) **1985**, *62*, 1 and references cited herein. (b) Aalten, H. L.; vanKoten, G.; Goubitz, K.; Stam, C. H. *J. Chem. Soc., Chem. Commun.* **1985**, 1252.

(4) (a) Figgis, B. N.; Martin, R. L. *J. Chem. Soc.* **1956**, 3837. (b) Catterick, J.; Hursthouse, M. B.; Thornton, P.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1977**, 223. (c) Cotton, F. A.; Duraj, S. A.; Roth, W. J. *Organometallics* **1985**, *4*, 1174.

(5) (a) Poumbga, C.; Daniel, C.; Benard, M. *Inorg. Chem.* **1990**, *29*, 2387. (b) Edema, J. J. H.; Gambarotta, S. *Comments Inorg. Chem.*, in press. (c) Edema, J. J. H.; Gambarotta, S.; Meetsma, A.; van Bolhuis, F.; Spek, A. L.; Smeets, W. J. J. *Inorg. Chem.* **1990**, *29*, 2147. (d) Wielstra, Y.; Gambarotta, S.; Spek, L. A.; Smeets, W. J. J. *Organometallics* **1990**, *9*, 2142.

(6) Folkesson, B.; Larsson, R. *Acta Chem. Scand., Ser. A* **1979**, *33*, 347.

(7) (a) Cotton, F. A.; Millar, M. *J. Am. Chem. Soc.* **1977**, *99*, 7886. (b) Cotton, F. A.; Lewis, G. E.; Mott, G. N. *Inorg. Chem.* **1983**, *22*, 560. (c) Cotton, F. A.; Diebold, M. P.; Shim, I. *Inorg. Chem.* **1985**, *24*, 1510.

(8) Cotton, F. A.; Extine, M. W.; Falvello, L. R.; Lewis, D. B.; Lewis, G. E.; Murillo, C. A.; Schwotzer, W.; Tomas, M.; Troup, J. M. *Inorg. Chem.* **1986**, *25*, 3505.

(9) Gelmini, L.; Armstrong, W. H. *J. Chem. Soc., Chem. Commun.* **1989**, 1904.

(10) (a) Edema, J. J. H.; Stauthamer, W.; vanBolhuis, F.; Gambarotta, S.; Smets, W. J. J.; Spek, A. L. *Inorg. Chem.* **1990**, *29*, 1302. (b) Edema, J. J. H.; Meetsma, A.; van Bolhuis, F.; Gambarotta, S. *Inorg. Chem.* **1991**, *30*, 2056. (c) Edema, J. J. H.; Gambarotta, S.; Meetsma, A.; Khan, S. Manuscript in preparation.

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