easily differentiate (or set up dynamic equilibria between) the various conformers seen from the van der Waals energy calculations. Some of these conformers are expected to have different enough local chemical environments for the central methylene and bridging ethylene protons to give rise to the ^{1}H NMR spectra seen in Figure 3.[8]

The qualitative, almost quantitative, agreement of the simple van der Waals energy calculations with the solid-state structures and solution dynamics is rather impressive and opens the door for more detailed NMR studies into these and other eHTP complexes. We are currently examining the reactions of 3 relative to those of mononuclear model complexes to see if this type of binuclear system can exhibit cooperative behavior between the metal centers for C–C bond-forming reactions in alkenes.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (Grant CHE-86-13089) for research support. We also acknowledge Monsanto Co. for a Young Faculty Research Support Grant. The assistance of the Washington University High-Resolution NMR Service Facility, funded in part through NIH Biomedical Research Support Shared Instrument Grant 1-S10-RR02004 and a gift from the Monsanto Co., is gratefully acknowledged.

Registry No. 3 (PF_6^- salt), 106973-26-6; **3a**, 106905-68-4; **3b**, 106973-25-5.

Supplementary Material Available: Figure of the full van der Waals energy map and tables of anisotropic thermal parameters, complete bond distances, and complete bond angles for both **3a** and **3b** (9 pages); tables of observed vs. calculated structure factors for both **3a** and **3b** (35 pages). Ordering information is given on any current masthead page.

---

(8) The cobalt complex (2) also exhibits marked solvent dependencies (although no anion effects have been observed) for its ^{1}H NMR spectra. We are currently concluding detailed two-dimensional studies on the cobalt system and plan to explore the nickel system in more detail: D'Avignon, A.; Askham, F. R.; Stanley, G. G., manuscript in preparation (cobalt system).

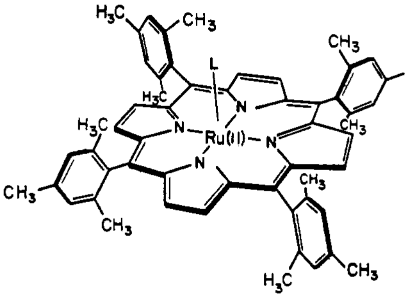
Contribution from the Department of Chemistry,
University of British Columbia,
Vancouver, British Columbia, Canada V6T 1Y6

Synthesis and Reactivity of Five-Coordinate (Porphinato)(tertiary phosphine)ruthenium(II) Complexes

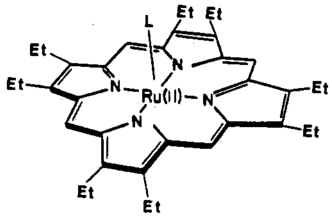
Chand Sishta, Mark J. Camenzind, Brian R. James,*
and David Dolphin*

Received December 5, 1986

Coordinatively unsaturated ruthenium porphyrin complexes such as [Ru(porp)]$_2$ (porp = dianion of 2,3,7,8,12,13,17,18-octaethylporphyrin (OEP) or 5,10,15,20-tetraphenylporphyrin (TPP)),[1] K$_2$[Ru(porp)] (porp = OEP or 5,10,15,20-tetratolylporphyrin dianion),[2] Ru(TMP) (TMP = dianion of 5,10,15,20-tetramesitylporphyrin),[3] Ru(OEP)R (R = $CHCH_3$ and C_2H_5,[4] CH_3 and C_6H_5[5]) and the in situ hydride[6] [RuH(TTP)]$^-$ have been reported recently. This note describes the synthesis, characterization, and some chemistry of the analytically pure complexes Ru(porp)(PR$_3$) (**2**, porp = TMP, R = *n*-Bu; **4**, porp = OEP, R = Ph); such 16-electron species, formed in situ by dissociation equilibria involving Ru(porp)(PR$_3$)$_2$,[7,8] have been implicated as intermediates in catalytic oxidation of phosphines[8] and decarbonylation of aldehydes.[9] Reaction of **2** or **4** with CO or PR$_3$ gives the expected six-coordinate derivatives, while aerobic treatment with HBr gives RuBr(porp)(PR$_3$); **2** and **4** are unreactive toward O_2, N_2, H_2, and aldehydes, and the implications of this nonreactivity for the reported catalysis are discussed.



2, L = *n*-Bu$_3$P



4, L = PPh$_3$

Experimental Section

^{1}H and ^{31}P NMR spectra were obtained in C_6D_6 in vacuo, with Varian XL-300 and Bruker WP-80 and WH-400 spectrometers, and shifts are reported relative to Me_4Si or 85% H_3PO_4, downfield shifts being positive. Visible spectra were run on a Cary 17D spectrophotometer.

Ru(TMP)(*n*-Bu$_3$P)$_2$ (1). The carbonyl Ru(TMP)(CO) (170 mg, 0.19 mmol), prepared by a literature method,[10] was dissolved in 20 mL of CH_2Cl_2 under N_2, and *n*-Bu$_3$P (0.34 mL, 1.4 mmol) was added. The solution was refluxed under N_2 until the visible spectrum of the carbonyl (λ_{max} 412, 524 nm) changed to that of **1**. After reduction of the solution volume to 5 mL by evaporation, dropwise addition of MeOH (15 mL) precipitated a purple powder that was filtered off, washed with MeOH, and dried under vacuum (200 mg, 84%). Anal. Calcd for $C_{80}H_{106}N_4P_2Ru$: C, 74.67; H, 8.30; N, 4.35. Found: C, 74.63; H, 8.22; N, 4.37. ^{1}H NMR: δ 8.43 s (8 H, pyrrole H), 7.23 s (8 H, *m*-H), 2.48 s (12 H, *p*-CH$_3$), 2.43 s (24 H, *o*-CH$_3$), 0.54 m (12 H, CH_2CH_3), 0.46 t (18 H, CH_2CH_3), −0.44 br (12 H, PCH_2CH_2), −1.79 br, t (12 H, PCH_2). ^{31}P NMR: δ −0.38 s. UV/visible (CH_2Cl_2): λ_{max} 437, 530, 562 nm.

Ru(TMP)(*n*-Bu$_3$P) (2). Complex **1** (60 mg, 0.05 mmol), on pyrolysis for 1 h at 270 °C under a 4×10^{-5} Torr vacuum loses phosphine and forms **2** quantitatively. Anal. Calcd for $C_{68}H_{79}N_4PRu$: C, 75.31; H, 7.34; N, 5.17. Found: C, 75.05; H, 7.33; N, 5.20. ^{1}H NMR: δ 8.45 s (8 H, pyrrole H), 7.29 s (4 H, *m*-H), 7.12 s (4 H, *m*-H), 2.63 s (12 H, *p*-CH$_3$), 2.47 s (12 H, *o*-CH$_3$), 1.72 s (12 H, *o*-CH$_3$), 0.43 m (15 H, CH_2CH_3), −0.64 m (6 H, PCH_2CH_2), −1.54 m (6 H, PCH_2). ^{31}P NMR: δ 53.09 s. UV/visible (CH_2Cl_2): λ_{max} 410, 498, 523 nm.

Ru(OEP)(PPh$_3$)$_2$ (3). Complex **3** was prepared according to the literature procedure.[7] ^{1}H NMR: δ 9.12 s (4 H, meso H), 6.57 t (6 H, *p*-H), 6.36 m (12 H, *m*-H), 4.36 m (12 H, *o*-H), 3.75 q (16 H, CH_2), 1.89 t (24 H, CH_3). ^{31}P NMR: δ 8.31 s.

---

(1) Collman, J. P.; Barnes, C. E.; Swepston, P. N.; Ibers, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 3500.

(2) Collman, J. P.; Brothers, P. J.; McElwee-White, L.; Rose, E.; Wright, L. J. *J. Am. Chem. Soc.* **1985**, *107*, 4570.

(3) Camenzind, M. J.; James, B. R.; Dolphin, D. *J. Chem. Soc., Chem. Commun.* **1986**, 1137.

(4) Collman, J. P.; McElwee-White, L.; Brothers, P. J.; Rose, E. *J. Am. Chem. Soc.* **1986**, *108*, 1332.

(5) James, B. R. Presented at the 24th International Conference on Coordination Chemistry, Athens, Greece, 1986; abstracts, p 28. Ke, M.; Rettig, S. J.; James, B. R.; Dolphin, D., to be submitted for publication.

(6) Collman, J. P.; Brothers, P. J.; McElwee-White, L.; Rose, E. *J. Am. Chem. Soc.* **1985**, *107*, 6110.

(7) Ariel, S.; Dolphin, D.; Domazetis, G.; James, B. R.; Leung, T. W.; Rettig, S. J.; Trotter, J.; Williams, G. M. *Can. J. Chem.* **1984**, *62*, 755.

(8) James, B. R.; Mikkelsen, S. R.; Leung, T. W.; Williams, G. M.; Wong, R. *Inorg. Chim. Acta* **1984**, *85*, 209.

(9) (a) Domazetis, G.; Tarpey, B.; Dolphin, D.; James, B. R. *J. Chem. Soc., Chem. Commun.* **1980**, 939. (b) Domazetis, G.; James, B. R.; Tarpey, B.; Dolphin, D. *ACS Symp. Ser.* **1981**, *No. 152*, 243.

(10) Groves, J. T.; Quinn, R. *Inorg. Chem.* **1984**, *23*, 3844.

0020-1669/87/1326-1181$01.50/0

Ru(OEP)(PPh$_3$) (4). This complex was made from **3** by the method described for **2** (2 h at 200 °C, 1×10^{-5} Torr, 1 mol equiv of PPh$_3$ being removed by sublimation). Anal. Calcd for $C_{54}H_{59}N_4PRu$: C, 72.40; H, 6.59; N, 6.26. Found: C, 72.49; H, 6.70; N, 6.13. ^{1}H NMR: δ 9.56 s (4 H, meso H), 6.50 t (3 H, *p*-H), 6.29 m (6 H, *m*-H), 4.21 m (6 H, *o*-H), 3.78 m (16 H, CH$_2$), 1.85 t (24 H, CH$_3$). These data agreed with those noted earlier for an impure sample[8] (see below). ^{31}P NMR: δ 58.59 s. The UV/visible spectrum is the same as that recorded for the species formed in situ.[7,8]

Results and Discussion

The synthesis of the five-coordinate complexes **2** and **4** demonstrates again the utility of the pyrolysis procedure in metalloporphyrin chemistry.[3] An earlier synthesis of **4** via amalgam reduction of RuBr(OEP)(PPh$_3$) gave a product contaminated with inorganics.[8] The lack of a porphyrin plane of symmetry in the five-coordinated species leads to ^{1}H NMR inequivalent *o*-CH$_3$ groups and meta protons within **2**[3] and inequivalent $-CH_2-$ protons of the ethyl groups within **4**.[8]

Both **2** and **4** can be stored under N$_2$ for months without decomposition, and in benzene at $\sim 10^{-3}$ M the species are unreactive toward 1 atm of N$_2$, H$_2$, and even dry (P$_2$O$_5$-treated) O$_2$. Solid samples of **2** and **4** are stable in air over days, but in solution, oxidation by air or undried O$_2$ occurs in minutes. ^{1}H NMR spectral changes show that **4** generates the Ru^{IV} μ-oxo species [Ru(OEP)OH]$_2$O,[11] a process clearly requiring the presence of trace moisture. The product from **2** has not been identified, but it is not Ru(TMP)(O)$_2$.[3,12] Earlier studies[8] showed that impure **4** in toluene reacted with O$_2$ (undried) to give [Ru(OEP)(OH)]$_2$O, which decomposed at 50 °C with trace water into RuO$_2$ and free-base porphyrin. The formation of the μ-oxo species during the O$_2$ oxidation of [Ru(OEP)]$_2$ has been similarly attributed to trace moisture.[13] These data highlight the trace water problem in this area. A stoichiometric O$_2$ oxidation of Ru(OEP)(PPh$_3$)$_2$ had been considered[8] to proceed via either (a) replacement of the O$_2$ of undetectable Ru(OEP)(PPh$_3$)O$_2$ as peroxide by attack of free PPh$_3$ or (b) a pathway that involves reaction of Ru(OEP)(PPh$_3$)O$_2$ with Ru(OEP)(PPh$_3$). The present findings rule out (b) but remain consistent with (a). An alternative outer-sphere O$_2$ oxidation of the bis(phosphine) species, assisted by protons (from water), that involved superoxide and then peroxide formation ($HO_2 \rightarrow {}^1/_2H_2O_2 + {}^1/_2O_2$) was ruled out on kinetic grounds,[8] but the rate data were preliminary, and more detailed studies using a controlled water content should be carried out to test for possible contribution from an outer-sphere process.

Both five-coordinate complexes react rapidly in benzene (10^{-3} M) with CO to give Ru(porp)(PR$_3$)CO[14] and with 1 equiv of the appropriate phosphine to give the precursor bis(phosphine) species. Of interest in a catalytic context, neither **2** or **4** in benzene show reactivity toward benzaldehyde even at 100 °C in sealed tubes. Solutions of Ru(TPP)(PPh$_3$)$_2$ containing added *n*-Bu$_3$P are extremely effective for catalytic decarbonylation of aldehydes;[9] a radical mechanism, although poorly defined, has been established,[9] and loss of CO (from Ru(porp)(PR$_3$)CO formed via aldehyde decarbonylation) according to demonstrated equilibria[7] such as eq 1 was considered as a possible step in all the overall catalysis.

$$\mathrm{Ru(porp)(PR_3)CO + PR_3 \rightleftharpoons Ru(porp)(PR_3)_2 + CO} \quad (1)$$

The present data show that any such carbonyl complex is unlikely to be formed by a purely thermal (or laboratory-light-induced) reaction of the aldehyde with a (porphinato)(phosphine)ruthenium(II) species. Attempts to synthesize Ru(TPP)(PPh$_3$) by vacuum pyrolysis of Ru(TPP)(PPh$_3$)$_2$ simply led to sublimation of the bis(phosphine) complex; this behavior was unexpected, in that the degree of dissociation of PPh$_3$ from the Ru(porp)(PPh$_3$)$_2$ complexes in toluene was greater for the TPP than for the OEP systems.[7]

Treatment of solutions of **2** or **4** with HBr(g) or 48% aqueous HBr under aerobic conditions gives high yields of RuBr(TMP)(*n*-Bu$_3$P)[15] or RuBr(OEP)(PPh$_3$),[16] respectively. Aerobic treatment of Ru(porp)(PR$_3$)$_2$ complexes with HX has proved useful previously for the synthesis of Ru^{III} porphyrin halide species, but the oxidation process concomitantly generates phosphine oxide, which has to be removed by chromatography.[8,16] Use of the five-coordinate precursors obviates the necessity of the separation procedure.

Finally, ^{1}H NMR and ^{31}P NMR studies show (a) that there is no tendency of **2** or **4** in solution to dissociate a phosphine to give Ru(TMP)[3] or [Ru(OEP)]$_2$,[1] respectively, and (b) that 1:1 mixtures of the mono- and bis(phosphine) species **3** and **4** undergo fast exchange of phosphine, while mixtures of **1** and **2** do not.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada and the National Institutes of Health (Grant No. AM 17989) for research grants and Johnson Matthey Ltd. for the loan of Ru.

---

(11) Collman, J. P.; Barnes, C. E.; Brothers, P. J.; Collins, T. J.; Ozawa, T.; Gallucci, J. C.; Ibers, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 5151.

(12) Groves, J. T.; Quinn, R. *J. Am. Chem. Soc.* **1985**, *107*, 5790.

(13) Collman, J. P.; Barnes, C. E.; Collins, T. J.; Brothers, P. J.; Gallucci, J.; Ibers, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 7030.

(14) (a) ^{1}H NMR for Ru(TMP)(*n*-Bu$_3$P)CO: δ 8.68 s (8 H, pyrrole H), 7.30 s (4 H, *m*-H), 7.02 s (4 H, *m*-H), 2.68 s (12 H, *o*-CH$_3$), 2.45 s (12 H, *p*-CH$_3$), 1.53 s (12 H, *o*-CH$_3$), 0.43 br (15 H, CH$_2$CH$_3$), −0.95 br (6 H, PCH$_2$C*H*$_2$), −2.08 s (6 H, PCH$_2$). (b) Ru(OEP)(PPh$_3$)(CO) has been synthesized previously: Barley, M.; Becker, J. Y.; Domazetis, G.; Dolphin, D.; James, B. R. *Can. J. Chem.* **1983**, *61*, 2389.

(15) RuBr(TMP)(*n*-Bu$_3$P). Anal. Calcd for $C_{68}H_{79}N_4BrPRu$: C, 70.15; H, 6.84; N, 4.81; Br, 6.86. Found: C, 69.88; H, 6.81; N, 4.62; Br, 6.68. UV/visible (CH$_2$Cl$_2$): λ_{max} 347, 425, 535 nm.

(16) James, B. R.; Dolphin, D.; Leung, T. W.; Einstein, F. W. B.; Willis, A. C. *Can. J. Chem.* **1984**, *62*, 1238.

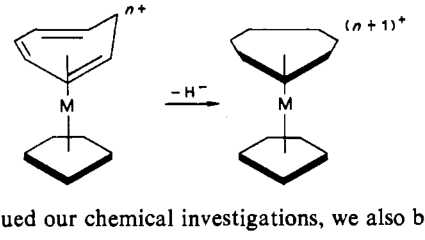
Contribution from the Department of Chemistry,
University of Minnesota, Minneapolis, Minnesota 55455

Synthesis, Reactivity, and Electrochemical Characterization of $[(\eta^5\text{-}C_5H_5)Ru(\eta^7\text{-}C_7H_7)](PF_6)_2$ and $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}C_7H_8)](PF_6)$

Amy M. McNair, David C. Boyd, David A. Bohling,
Thomas P. Gill, and Kent R. Mann*

Received June 18, 1986

During the last few years, we have been interested in the syntheses and properties of new [CpM(L)$_3$]$^+$ complexes (Cp = η^5-cyclopentadienyl; M = Fe, Ru; L$_3$ = 6-electron-donor ligand) via the photolytically generated [CpM(S)$_3$]$^+$ solvato complexes (M = Fe, S = CH$_2$Cl$_2$; M = Ru, S = CH$_3$CN).[1,2] One new complex that we synthesized in high yields via the photochemical route is [CpFe(CHT)](PF$_6$) (CHT = η^6-cycloheptatriene).[3] The relative ease of obtaining this material and its favorable chemical properties suggested that it would be a good candidate for hydride abstraction studies designed to convert the coordinated CHT ligand to the coordinated tropylium (trop$^+$) ligand:



As we pursued our chemical investigations, we also became in-

---

(1) Gill, T. P.; Mann, K. R. *Inorg. Chem.* **1983**, *22*, 1986.

(2) Gill, T. P.; Mann, K. R. *Organometallics* **1982**, *1*, 485.

(3) Gill, T. P.; Mann, K. R. *J. Organomet. Chem.* **1981**, *216*, 65.

0020-1669/87/1326-1182$01.50/0