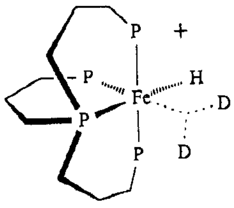
the η^2-bound HD is approximately 133 ms. Crabtree and Lavin[13] have noted that the T_1 of η^2-bound HD is significantly longer than that of the η^2-H_2 due to the smaller magnetic moment of the deuterium nucleus. Again, saturation-transfer experiments indicate that there is still significant exchange between the classically bound and η^2-bound environments at this temperature, and the measured T_1 values must have a contribution from exchange averaging.

There are two stereoisomers possible for a H/η^2-H_2 trihydride complex i.e. with the classically bonded hydride cis or trans to the apical phosphorus. Only one isomer is observed in the ${}^1H$ NMR spectrum of **4** at low temperature, and on the basis of ${}^{31}P$–${}^{1}H$ coupling constants, we assign this as the stereoisomer with the hydride trans to the apical phosphorus. In the dihydride, **1**, the ${}^{31}P$–${}^{1}H$ coupling constants uniquely define the assignment of the two iron-bound hydrides[14] with cis-${}^{31}P$–${}^{1}H$ coupling to the terminal phosphorus atoms being relatively large (45–70 Hz) and trans-${}^{31}P$–${}^{1}H$ coupling to the terminal phosphorus atoms being significantly smaller (ca. 30 Hz). The corresponding coupling constants to the apical phosphorus are smaller than those to the terminal nuclei by approximately 50%. The hydride in **4** exhibits three large ${}^{31}P$ couplings of ca. 56 Hz, and this locates it trans to the apical phosphorus.



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As with other iron complexes of molecular hydrogen, the η^2-bound H_2 in **2** is substituted readily with better ligands such as halides[15] and alkane- and arenethiolate[16] to give substituted iron P_4 hydrides.

Acknowledgment. We gratefully acknowledge financial support from the Australian Research Grants Scheme.

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(14) In the dihydride **1**, the hydride located trans to the apical phosphorus exhibits a triplet splitting (60.0 Hz) to the equivalent axial ${}^{31}P$ nuclei, another relatively large coupling (47.9 Hz) to the terminal equatorial ${}^{31}P$ nucleus, and a coupling of 11.9 Hz to the apical phosphorus. In contrast, the other hydride exhibits a triplet splitting (70.9 Hz) due to the terminal diaxial ${}^{31}P$ nuclei, a coupling of 14.3 Hz to the trans terminal phosphorus and a coupling of only 33.5 Hz to the cis-apical phosphorus.

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Synthesis and Characterization of $Rh_2(O_2CCH_3)_3[\{C_6H_2(OMe)_3\}_2P\{C_6H_2(OMe)_2O\}](MeOH)$ with a Novel Tridentate Ligand Derived from Tris(2,4,6-trimethoxyphenyl)phosphine

It is well-known that metal phosphine complexes are good catalyst precursors in important reactions such as hydrogenation, hydroformylation, and polymerization.[1] The investigation of bulky and labile phosphine ligands is especially interesting due to the formation of reactive coordinatively unsaturated molecules.[2] One of our recent research interests is to explore the chemistry of the unusually large and basic phosphine ligand tris(2,4,6-trimethoxyphenyl)phosphine (TMPP) with low-valent metal centers.[3] Several other groups have reported the use of this phosphine in organic reactions[4] and in solid-state ${}^{31}P$ NMR studies.[5] The first TMPP complex that was prepared in our laboratories is $[Rh(TMPP)_2](BF_4)_2$, a novel Rh^{II} monomer possessing a chelating tridentate arrangement for the PR_3 ligand.[3a] Since both oxygen and phosphorus atoms are good donors, one may envision a variety of possible multidentate coordination modes for this ligand such as chelating tridentate (**1**), bridging bidentate (**2**), or bridging and chelating tridentate (**3**). The use of this highly flexible ligand in the series of complexes $[Rh(TMPP)_2]^{n+}$ (n = 1, 2, 3), all exhibiting some variation of structure **1** above, afforded us the rare opportunity to probe the geometrical preferences of a metal center as a function of the electronic configuration.[6] We were

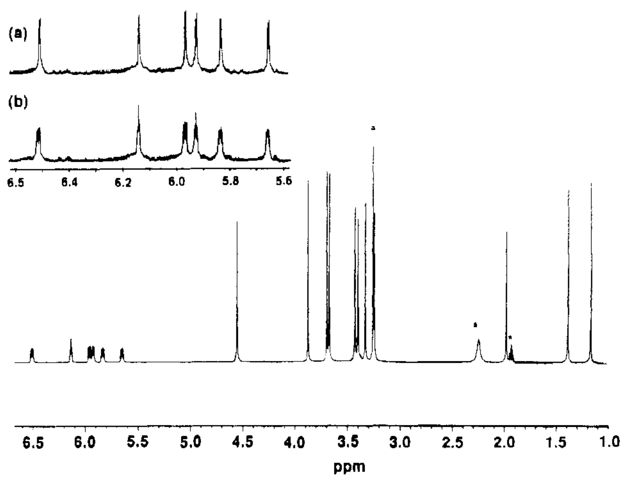

Figure 1. Room-temperature 300-MHz ${}^1H$ NMR spectrum of **1** in CD_3CN (peak a is methanol; an asterisk marks the CD_3CN impurity). The inset shows the metal proton region at 500 MHz with (a) phosphorus nuclei decoupled and (b) phosphorus nuclei nondecoupled.

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(2) See for example: (a) Osborn, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, G. *J. Chem. Soc. A* **1966**, 1711. (b) Halpern, E. J.; Mislow, K. *J. Am. Chem. Soc.* **1967**, *89*, 5224. (c) Alyea, E. C.; Malito, J. *J. Organomet. Chem.* **1988**, *340*, 119 and references therein. (d) Bowden, J. A.; Colton, R. *Aust. J. Chem.* **1971**, *24*, 2471. (e) Bennett, M. A.; Bramley, R.; Longstaff, P. A. *J. Chem. Soc., Chem. Commun.* **1966**, 806. (f) Ferguson, G.; Roberts, P. J.; Alyea, E. C.; Khan, M. *Inorg. Chem.* **1978**, *17*, 2965. (g) Darensbourg, D. J.; Darensbourg, M. Y.; Gob, L. Y.; Ludvig, M.; Wiegreffe, P. *J. Am. Chem. Soc.* **1987**, *109*, 7539. (h) Clark, H. C.; Hampden-Smith, M. J. *Coord. Chem. Rev.* **1987**, *79*, 229 and references therein. (i) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120.

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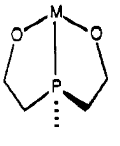

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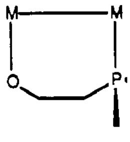

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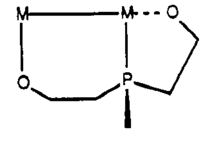

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intrigued by these results in monomer chemistry, and we became curious about what possibilities this ligand might have in higher nuclearity metal compounds. We therefore undertook a study of the reaction between the well-known dirhodium tetraacetate complex and TMPP. This work resulted in the synthesis of an unusual binuclear compound containing a bridging and chelating form of the TMPP ligand, which lends further support to our predictions regarding the flexibility and diverse reactivity of this interesting ligand.

The title complex is prepared by refluxing a suspension of $Rh_2(\mu\text{-}O_2CCH_3)_4(MeOH)_2$ (0.10 g, 0.2 mmol) and TMPP (0.21 g, 0.4 mmol) in ethanol (20 mL) for 4 h. Upon evaporation, the resulting green solution yields an impure residue, which may be extracted with a 1:1 mixture of methanol–diethyl ether to give a pure sample of $Rh_2(\mu\text{-}O_2CCH_3)_3(O\text{-TMPP})(MeOH)$ (**1**) where *O*-TMPP denotes the oxygen-metalated form of the ligand. Crystals were obtained by slow evaporation of the solution in air (yield: 0.118 g, 64%).

The compound has been fully characterized by ^1H NMR,[7] $^{31}P\{^1H\}$ NMR, and electronic spectroscopies[8] as well as by electrochemistry and a single-crystal X-ray analysis.[9] The ^1H NMR spectrum of a powder sample of **1** revealed that the TMPP ligand is bonded in a completely unsymmetrical fashion, thus rendering all six meta protons and eight methoxy groups inequivalent. The absence of a ninth methoxy resonance suggested that a demethylation reaction had occurred, which was later confirmed by the solid-state structure (vide infra). Figure 1 displays a 300-MHz ^1H NMR spectrum of **1** in CD_3CN; the inset shows an expanded view of the phosphorus-decoupled (a) and undecoupled (b) meta resonances taken from a 500-MHz ^1H NMR spectrum. The $^{31}P\{^1H\}$ spectrum in CD_3CN exhibits a doublet at $\delta = -9.8$ ppm with $J(^{103}Rh-^{31}P) = 159$ Hz.[10]

The identity of $Rh_2(O_2CCH_3)_3(O\text{-TMPP})(MeOH)$ was confirmed by a single-crystal X-ray structure. As Figure 2 shows, the molecule consists of a dirhodium unit bridged by three acetate ligands and one TMPP ligand that forms two separate metallacycle rings with the rhodium atoms. In this arrangement, the phosphorus atom occupies an equatorial position, and one *o*-methoxy group has demethylated to form an alkoxide group. This type of dealkylation reaction has been noted for other phosphine ligands with *o*-methoxy phenyl substituents.[11] We have also documented this reaction pathway for TMPP in monomeric Rh(III) systems.[12] The exact fate of the CH_3 moiety in this particular instance is not known, but it is reasonable to expect that it is involved in the esterification of an acetate ligand. The same rhodium center to which the phosphorus atom is bonded also binds axially to the oxygen of an *o*-methoxy group. This combination of chelating and bridging ligation is very unusual but is not without precedence. Lahuerta et al. studied the orthometalation reactions of $(o\text{-}BrC_6F_5)P(C_6H_5)_2$ with dirhodium tetraacetate, and several products exhibiting the η^3,μ-bonding mode were isolated and structurally characterized.[13] Earlier, Cotton and co-workers had reported a novel orthometalation of PPh_3 with $Rh_2(\mu\text{-}O_2CCH_3)_4$, although in this case the ligand assumes a η^2,μ arrangement.[14] More recently, Lahuerta has studied the PPh_3 reaction in detail.[15] Related chemistry occurs with mixed alkyl–arylphosphines as demonstrated by Morrison and Tocher.[16]

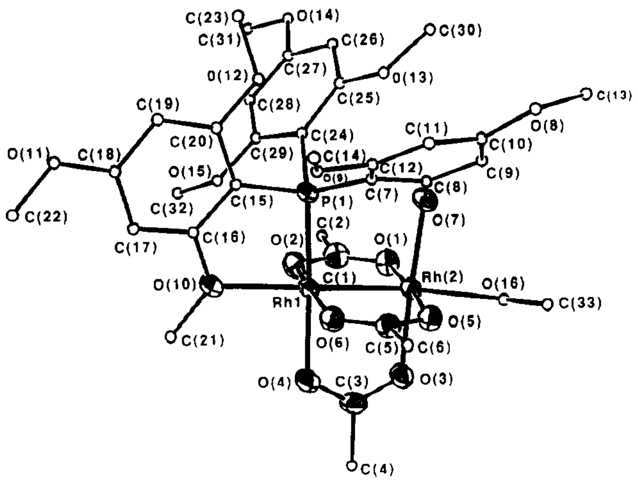

Figure 2. ORTEP representation of **1** with 50% probability ellipsoids. Phenyl group carbon atoms are depicted by arbitrarily small spheres for clarity.

Distances and angles in the molecule are within typical ranges. As expected, the metalated oxygen atom is bonded much more strongly (Rh(1)–O(7) = 2.048 (2) Å) than the axial ether group (Rh(1)–O(10) = 2.351 (2) Å). The substantial distortions of angles about the phosphorus atom are a consequence of the formation of the five- and six-membered metallacycles Rh–P–C–C–O and Rh–Rh–P–C–C–O respectively. The Rh–Rh separation of 2.4228 (3) Å is similar to that observed for the parent tetraacetate complex $Rh_2(O_2CCH_3)_4(MeOH)_2$ (Rh–Rh = 2.377 Å).[17]

An electrochemical study of **1** revealed that a one-electron reversible oxidation is located at $E_{1/2} = +0.71$ V vs Ag/AgCl in THF and at +0.78 V in CH_3CN. Oxidative controlled-potential electrolysis of the complex in CH_3CN at 1.0 V is accompanied by a color change from green to deep orange-brown. Chemical oxidation was also carried out by the reaction of $Rh_2(O_2CCH_3)_3(O\text{-TMPP})(MeOH)$ and 1 equiv of $NOPF_6$ in CH_3CN. Attempts to isolate and fully characterize the resulting Rh_2^{5+} product are underway.

The reactivity of the title compound with H_2 and CO at 1 atm in CD_3CN was examined by ^1H NMR. Surprisingly, both spectra

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(6) Dunbar, K. R.; Haefner, S. C.; Pence, L. E. Manuscript in preparation.

(7) ^1H NMR in CD_3CN (δ): 3 $[O_2CCH_3]^-$ (1.19 s, 3 H; 1.40 s, 3 H; 2.00 s, 3 H); 8 $[OCH_3]$ (3.26 s, 3 H; 3.35 s, 3 H; 3.41 s, 3 H; 3.44 s, 3 H; 3.69 s, 3 H; 3.71 s, 3 H; 3.89 s, 3 H; 4.57 s, 3 H); 6 meta H (5.66 q, 1 H; 5.84 q, 1 H; 5.94 t, 1 H; 5.97 q, 1 H; 6.15 t, 1 H; 6.52 q, 1 H).

(8) UV–visible absorption spectrum in CH_3CN: [λ_{max}, nm (ϵ, $M^{-1}\,cm^{-1}$)]: 600 (174), 250 (33 700).

(9) The compound crystallizes as small parallelpipeds in the triclinic space group $P\bar{1}$ with $a = 13.730$ (3) Å, $b = 14.396$ (5) Å, $c = 11.921$ (5) Å, $\alpha = 109.65$ (2)°, $\beta = 95.65$ (2)°, $\gamma = 64.321$ (2)°, $V = 1997$ (1) Å^3, $Z = 2$, $d_{calcd} = 1.633$ g/cm^3, and μ(Mo Kα) = 9.251 cm^{-1}. A Nicolet P3/F diffractometer was used to collect a hemisphere of data ($+h,\pm k,\pm l$) in the range $4 \le 2\theta < 50°$ at 22 ± 2 °C; of the 7053 unique data, 6209 data with $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement. An absorption correction based on ψ scans was applied to the data; maximum and minimum transmission factors were 0.999 and 0.830. The agreement factor for averaged reflections was 0.012. Residuals of $R = 0.0504$ and $R_w = 0.0858$ were obtained after 451 parameters had refined to convergence. The quality-of-fit index is 2.933, and the largest shift/esd = 0.96.

(10) For the spectrum displayed in Figure 1, the sample contains methanol of crystallization (denoted with an a), which adds a ninth methyl resonance to the 3.2–3.5 ppm region as well as a broad OH resonance at 2.25 ppm.

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(12) For example, the Rh(III) complex $[Rh(TMPP)_2]^{3+}$ slowly converts in solution to $Rh(TMPP)[C_6H_2(OMe)_2OP\{C_6H_2(OMe)_3\}_2]^{2+}$. Dunbar, K. R.; Haefner, S. C. Manuscript in preparation.

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exhibit similar changes in the structurally sensitive meta proton region of the TMPP ligand. Detailed studies of these and other small molecule reactions will be published in due course.[18]

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Supplementary Material Available: Tables of crystallographic data, atomic parameters, equivalent isotropic displacement parameters, bond distances, bond angles, and anisotropic thermal parameters (13 pages); a table of observed and calculated structure factors (35 pages). Ordering information is given on any current masthead page.

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Synthesis of $[Ru(CO)_2(Se_4)_2]^{2-}$. A Stable Anionic Ru^{2+} Polychalcogenide Complex

RuS_2 is one of the most active catalysts known for the hydrodesulfurization, HDS, of crude oil.[1,2] As with the other HDS catalysts (i.e. MoS_2, WS_2, and "CoMoS"), the mechanism of its action is currently unknown.[3] Although this challenge has driven the development of a great deal of Mo and W chemistry[4] with polysulfide ligands in an effort to find suitable model compounds for the surface of MoS_2, relatively little has been accomplished in the corresponding Ru/S chemistry. The Ru/S system has proven somewhat recalcitrant to study in the sense that, to date, no homoleptic Ru/S complexes have been isolated in pure form and/or structurally characterized. We are interested in the RuS_2/HDS problem from the standpoint of mimicking the active sites present in RuS_2. By exploring the fundamentals of Ru^{2+}/polychalcogenide chemistry, we aim to establish the currently unknown coordination preferences of this metal with HDS-relevant ligands. Thus far, the only Ru polychalcogenide complexes known are $[Ru(NH_3)_5]_2S_2^{4+}$,[5] $[CpRu(PR_3)_2]_2S_2^{2+}$,[6] $[MeCpRu(PPh_3)]_2S_x$ ($x = 4, 6$),[7] $Cp^*{}_2Ru_2(S_2)_2$,[8] $(Me_3P)_3RuS_7$,[9] $Ru(CO)_2(PPh_3)_2(S_2)$,[10] and $(bpy)_2RuS_5$, of which the last three have not been crystallographically characterized.[11] The only structurally characterized corresponding polyselenide complexes are the cationic $[CpRu(PPh_3)_2]_2Se_2^{2+}$ and $[MeCpRu(PPh_3)]_2(Se_2)_2^{2+}$.[12] The absence of homoleptic anionic Ru/Q_x (Q = S, Se, Te) complexes is probably due to their instability with respect to internal redox processes. Although Se ligands are not HDS-relevant, structures stabilized only by selenium ligands may emulate or represent difficult to isolate reactive intermediates in sulfur chemistry, and thus provide useful insight into the problem. We report here the synthesis and structural and spectroscopic characterization of the first stable anionic Ru/polyselenide complex, $[Ru(CO)_2(Se_4)_2]^{2-}$.

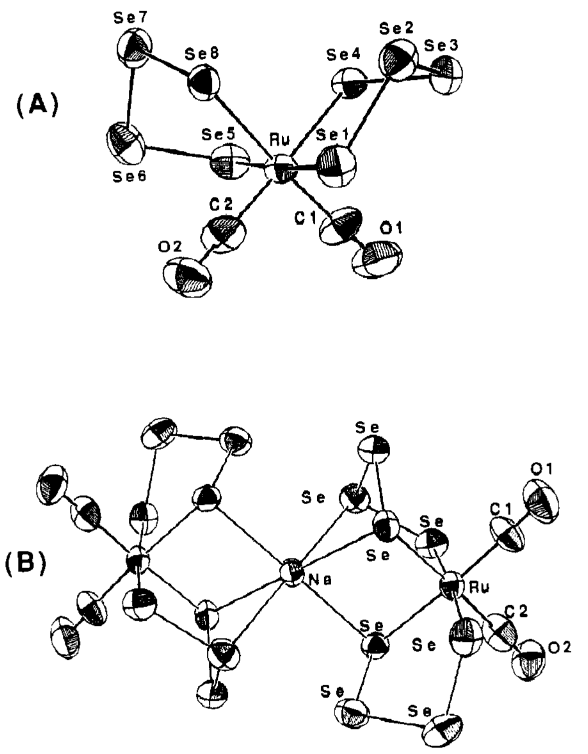

Figure 1. (A) ORTEP drawing of the $[Ru(CO)_2(Se_4)_2]^{2-}$ ion showing the labeling scheme. (B) Representation of the $[Na\{(Ru(CO)_2(Se_4)_2)\}_2]^{3-}$ portion of the structure showing the coordination environment of the Na^+ ion by two $[Ru(CO)_2(Se_4)_2]^{2-}$ ions. Selected bond distances (Å): Ru–C(1), 1.858 (8); Ru–C(2), 1.846 (8); Ru–Se(1), 2.517 (1); Ru–Se(4), 2.566 (1); Ru–Se(5), 2.513 (1); Ru–Se(8), 2.588 (1); Se(1)–Se(2), 2.346 (1); Se(2)–Se(3), 2.323 (1); Se(3)–Se(4), 2.353 (1); Se(5)–Se(6), 2.339 (1); Se(6)–Se(7), 2.315 (1); Se(7)–Se(8), 2.369 (1); C(1)–O(1), 1.132 (10); C(2)–O(2), 1.137 (10); Na–Se(2), 3.148 (1); Na–Se(4), 2.939 (1); Na–Se(8), 2.921 (1). Selected angles (deg): C(1)–Ru–C(2), 95.0 (2); Se(1)–Ru–Se(4), 97.32 (4); Se(1)–Ru–Se(5), 174.95 (5); Se(1)–Ru–Se(8), 79.45 (4); Se(4)–Ru–Se(5), 80.72 (4); Se(4)–Ru–Se(8), 93.58 (3); Se(5)–Ru–Se(8), 95.99 (4); Se(1)–Se(2)–Se(3), 99.25 (5); Se(2)–Se(3)–Se(4), 97.19 (5); Se(5)–Se(6)–Se(7), 99.64 (5); Se(6)–Se(7)–Se(8), 97.28 (5); C(1)–Ru–Se(1), 93.4 (2); C(1)–Ru–Se(4), 85.4 (2); C(1)–Ru–Se(5), 91.1 (2); C(1)–Ru–Se(8), 172.6 (2); C(2)–Ru–Se(1), 89.4 (2); C(2)–Ru–Se(4), 173.2 (2); C(2)–Ru–Se(5), 92.5 (2); C(2)–Ru–Se(8), 86.9 (2).

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