In summary, a straightforward route is offered for in situ generation of oxoiron(IV) porphyrin compounds, and the direct oxo transfer chemistry for trialkylamine *N*-oxide oxidation of iron(II) porphyrins is demonstrated. Further characterization of the coordination and redox chemistry of trialkylamine *N*-oxides is in progress.

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Isolation and Structure of the Novel Dirhodium(II) Compound $Rh_2(dmpm)_2[(C_6H_5)_2P(C_6H_4)]_2Cl_2$ with Bridging Bis(dimethylphosphino)methane and Ortho-Metalated Triphenylphosphine Ligands

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The preparation[1-3] and electronic structure[4] of binuclear rhodium(II) complexes possessing a Rh–Rh single bond have been topics of considerable interest in recent years. Much of the research that has been conducted in these areas focuses upon the spectral and chemical properties of the dirhodium tetracarboxylate compounds, species which form axial adducts with a wide variety of σ-donor and π-acid ligands. The metathesis reactions of the bridging carboxylate groups have been well-investigated. For example, the acetate groups in $Rh_2(\mu\text{-}O_2CCH_3)_4L_2$ can be replaced by other $R'CO_2^-$ groups or by a variety of different ligands such as sulfate,[5] dihydrogenphosphate,[6] amidate,[7] or 2-oxypyridine anions.[2] Quite often, the products isolated from these reactions contain four bridging ligands of the same type, viz., $[Rh_2(SO_4)_4(H_2O)_2]^{4-}$, $Rh_2(H_2PO_4)_4(H_2O)_2$, $Rh_2(HNOCCH_3)_4(H_2O)_2$, and $Rh_2(mhp)_4$ (mhp = 2-methylhydroxypyridinato).

Among the few documented examples of dirhodium(II) compounds containing more than one kind of bridging groups are the structurally characterized compounds $Rh_2(O_2CCH_3)_2(O_2CCPh_3)_2(CH_3CN)_2{\cdot}C_7H_8$[8] and $Rh_2(O_2CCH_3)_2(mhp)_2(Im)$[9] and the amidato–carboxylato complexes reported by Bear et al.[7] Several additional mixed-ligand $Rh^{II}Rh^{II}$ compounds of an unusual type were recently prepared in our laboratories from the reactions of $Rh_2(\mu\text{-}O_2CCH_3)_4$ with tertiary arylphosphines. When the phosphine $P(O\text{-}BrC_6F_4)Ph_2$ (PCBr) was used, four major products were formed, each of which possesses several $\mu\text{-}O_2CCH_3$ groups and at least one ortho-metalated PCBr ligand.[10,11] An earlier study of the reaction between PPh_3 and $Rh_2(O_2CCH_3)_4$ in refluxing acetic acid led to the isolation of $Rh_2(O_2CCH_3)_2[(C_6H_5)_2P(C_6H_4)]_2(L)_2$ (L = CH_3COOH, C_5H_5N), a molecule containing two $\mu\text{-}O_2CCH_3$ ligands in a cisoid arrangement and two bridging $o\text{-}(Ph_2P)C_6H_4^-$ anions.[12] It is the reactivity of this ortho-metalated compound which is the topic of the present communication.

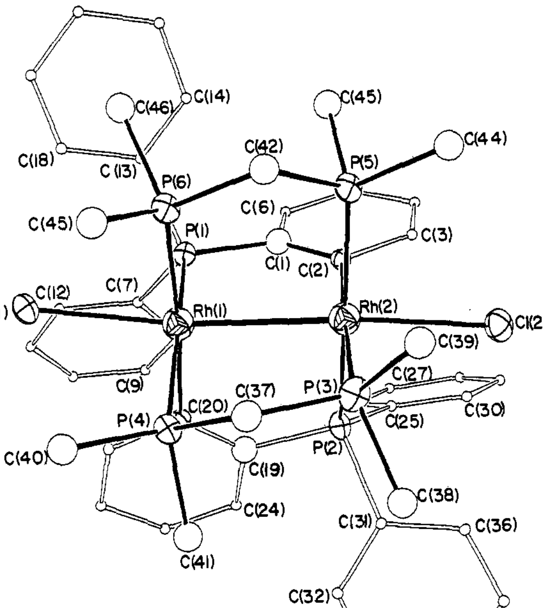

Figure 1. ORTEP drawing of the $Rh_2(dmpm)_2[(C_6H_5)_2P(C_6H_4)]_2Cl_2$ molecule with the atom labeling scheme. Some important distances (Å) and angles (deg): Rh(1)–Rh(2), 2.770 (3); Rh(1)–Cl(1), 2.561 (6); Rh(2)–Cl(2), 2.527 (6); Rh(1)–P(1), 2.345 (6); Rh(1)–P(4), 2.302 (6); Rh(1)–C(20), 2.07 (2); Rh(2)–C(2), 2.09 (2); P(1)–C(1), 1.80 (2); P(1)–C(7), 1.89 (2); P(4)–C(37), 1.82 (2); P(4)–C(40), 1.83 (2); C(1)–C(2), 1.41 (3); C(7)–C(8), 1.40 (3); Rh(2)–Rh(1)–Cl(1), 172.5; Rh(2)–Rh(1)–P(1), 89.0 (2); Rh(2)–Rh(1)–P(4), 91.1 (2); Rh(2)–Rh(1)–C(20), 90.1 (6); Cl(1)–Rh(1)–P(1), 91.8 (2); Cl(1)–Rh(1)–P(4), 89.7 (2); Cl(1)–Rh(1)–C(20), 97.4 (6); P(1)–Rh(1)–P(4), 167.4 (2); Rh(1)–Rh(2)–Cl(2), 171.4 (1); P(3)–C(37)–P(4), 106 (1).

We have found that the acetate ligands in $Rh_2(O_2CCH_3)_2(PPh_2C_6H_4)_2$ and also in $Rh_2(O_2CCH_3)_4$[13] can be labilized by using trimethylsilyl chloride. This synthetic approach was first reported by McCarley and co-workers[14] and by Green et al.,[15] who found that $SiMe_3Cl$ acts as a mild and selective reagent for the replacement of μ-acetato groups in $Mo_2(O_2CCH_3)_4$.

For the past several years, we have endeavored to demonstrate the general utility of this type of reaction as a method for the high-yield synthesis of new bimetallic compounds of Mo,[16] W,[17]

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Ru,[18] and Os[19] from readily available starting materials that possess oxygen donor or mixed oxygen–nitrogen donor ligand sets. We have now extended this chemistry to include reactions of dirhodium compounds; the specific reaction reported here, eq 1,

$$Rh_2(O_2CCH_3)_2(PPh_2C_6H_4)_2 + 2Me_3SiCl + 2dmpm \xrightarrow[\Delta]{THF} Rh_2(dmpm)_2(PPh_2C_6H_4)_2Cl_2 + 2Me_3SiOOCH_3 \quad (1)$$

proceeds smoothly through a series of color changes from blue, which is the THF adduct $Rh_2(OCCH_3)_2(PPh_2C_6H_4)_2(THF)_2$, to deep green after addition of the Me_3SiCl, and finally to bright red upon addition of 2 equiv of dmpm. The red color persists even after prolonged reflux, and subsequent workup of the solution yields $Rh_2(dmpm)_2[(C_6H_5)_2P(C_6H_4)]Cl_2$ as a pale microcrystalline material in ~85% yield. The product was recrystallized from CH_2Cl_2–hexane to afford dark red crystals of $Rh_2(dmpm)_2[(C_6H_5)_2P(C_6H_4)]_2Cl_2{\cdot}CH_2Cl_2$ which were used for vibrational and electronic spectroscopy, electrochemistry, and a single-crystal X-ray structural determination.

The IR spectrum of the title compound revealed the presence of both coordinated dmpm and ortho-metalated triphenylphosphine but no bands attributable to acetate ligands. The UV-visible spectrum of $Rh_2(dmpm)_2(PPh_2C_6H_4)Cl_2$, recorded in CH_2Cl_2 solution, exhibits several characteristic features at λ_{max}: (mn, ϵ) 550 (740); 520 sh; 368 (16 400); 300 (9370). A cyclic voltammogram of the product in 0.2 M Bu_4NPF_6–CH_2Cl_2 shows the presence of one couple at $E_{1/2} = +0.85$ V vs. Ag/AgCl which corresponds to the one-electron oxidation $Rh^{II}Rh^{II} \rightleftharpoons Rh^{II}Rh^{III}$. This redox behavior is typical of binuclear rhodium(II) complexes.[2]

The identity of $Rh_2(dmpm)[(C_6H_5)_2P(C_6H_4)]_2Cl_2$ was confirmed by a crystallographic study following general procedures described elsewhere.[20-22] The molecule, shown in Figure 1, consists of two Rh atoms bridged by two $Me_2PCH_2PMe_2$ ligands in a cis disposition and two o-$(Ph_2P)C_6H_4^-$ ligands that are arranged in the same head-to-tail manner as in the parent compound $Rh_2(O_2CCH_3)_2(PPh_2C_6H_4)_2L_2$. The axial chloride ligands complete the coordination sphere for an overall distorted octahedral geometry around each Rh atom (angles are in the range 89–92°). The Rh(1)–Rh(2)–Cl(axial) angles (av = 171.9°) do not deviate significantly from linearity unlike the Rh–Rh–L(axial) angles observed for the adducts $Rh_2(O_2CCH_3)_2(PPh_2C_6H_4)(L)_2$ (L = CH_3COOH, C_5H_5N) (Rh–Rh–L(av) = 162.8°). In the new compound, the axial Rh–Cl bonds are relatively short (2.561 (6) Å) and this correlates with the length of the Rh–Rh bond, which is 2.770 (3) Å, the longest distance ever observed for a dirhodium(II) compound. The corresponding M–M distances in the diacetate starting material $Rh_2(O_2CCH_3)_2(PPh_2C_6H_4)_2(L)_2$ are 2.508 (1) Å for L = CH_3COOH and 2.556 (2) Å for L = C_5H_5N, which are also quite long compared to the Rh–Rh distances found in the tetracarboxylate dirhodium compounds.[2]

The Rh–P distances are in the expected range, with the Rh–P distances trans to another phosphorus atom being shorter than those trans to a carbon atom, in accord with the expected order of the trans influence of M–P and M–C bonds. The average Rh–C bond distance of 2.08 (1) Å is quite normal. Additional important interatomic dimensions are listed in the caption for Figure 1.

The isolation of the Rh(II) dimer reported here has important consequences. It documents the existence of a previously unknown chemistry for dirhodium compounds containing bridging carboxylate ligands. The method outlined in this paper can be used to prepare, from readily available starting materials, unusual mixed-ligand complexes that possess an Rh_2^{4+} dinuclear core. Work that is currently under way in our laboratories has confirmed the general nature of this synthetic approach. A complete report of these results will be submitted later.

Acknowledgment. We thank the National Science Foundation for support.

Supplementary Material Available: Tables of crystallographic parameters, atomic positional parameters, and equivalent isotropic displacement parameters, bond distances and angles, and anisotropic thermal parameters (9 pages); table of observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

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Heats of Reaction of $Cp^*(PMe_3)Ir(R)(H)$ (R = C_6H_5, C_6H_{11}, and H) with HCl, CCl_4, CBr_4, and CH_3I. A Solution Thermochemical Study of the C–H Insertion Reaction

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A number of coordinatively unsaturated transition-metal complexes have been found to insert into carbon–hydrogen bonds,[1] leading to stable hydrido alkyl metal complexes as shown in eq 1. In such reactions, the sum of the M–H and M–C bond

$$M + R\text{–}H \rightarrow R\text{–}M\text{–}H \quad (1)$$

dissociation energies in R–M–H must be comparable to, or larger than, the energy of the alkane C–H bond which is broken. This is the "driving force" for C–H activation and must be on the order of 110 kcal/mol for reaction to occur.[2] Values have been obtained for some first-row transition-metal–alkyl (=30 kcal/mol) and metal–hydride(=60 kcal/mol) bond strengths,[3] but less information has been available for the second- and third-row metals. We now wish to report thermochemical studies which provide a precise value of the difference between the metal–carbon and metal–hydrogen bond energies in $Cp^*(PMe_3)Ir(H)(R)$ complexes and reasonable estimates for the absolute values of these and several other Ir–X bonds (X = H, Cl, Br, I, C_6H_{11}, and C_6H_5).

Relative M–C bond strength estimates for a number of alkyl groups in this series were determined previously by one of our

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