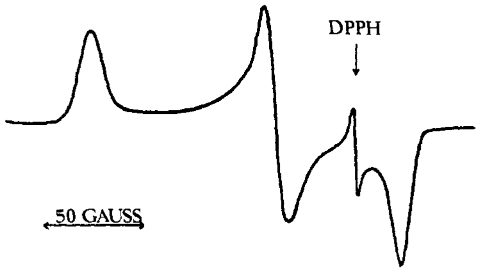


Figure 1. The esr spectrum of Rh^{II}(TPP) in chloroform at 77°K.

$(DMG)_4(PPh_3)_2$ (where DMG is the monoanion of dimethylglyoxime) is diamagnetic;[13] and low magnetic moments in some phosphine complexes have been attributed[11] to metal–metal interactions over 4 Å. Strong metal–metal interactions along axial positions at first appear unlikely in the tetraphenylporphyrins because of steric restrictions imposed by the phenyl groups,[15,16] but the possibility that the rhodium is out of the porphyrin plane, allowing a Rh–Rh interaction, cannot be excluded.

The ir of the rhodium(II) complex shows no carbonyl bands. The visible spectrum in chloroform has peaks at 418, 531, 568, and 601 nm. Shifts in the visible spectrum and esr spectrum in coordinating solvents lead us to tentatively assign the species in solution as four coordinate. Analysis of the complex has proved difficult owing to its tendency to retain varying amounts of solvent molecules in the solid state; such behavior is not unusual for metal porphyrins.[17] Molecular weight determination in chloroform indicates a monomeric species.

Stronger evidence for the formulation as a rhodium(II) complex comes from its reaction with hydrogen. In propanol or dimethylformamide (DMF) at 20°, the complex absorbs 0.5 mol of H_2 per Rh to give air-sensitive solutions which yield the diamagnetic rhodium(I) complex, $H[Rh(TPP)]\cdot 2H_2O$. (*Anal.* Calcd: C, 70.1; H, 4.4; N, 7.45; O, 4.4; Rh, 13.7. Found: C, 69.14; H, 4.42; N, 7.62; O, 4.70; Rh, 14.18.) The complex contains a titratable proton and has a molar conductance of 16.6 ohm^{-1} cm^2 at 5×10^{-4} *M* in DMF. Some 1:1 electrolytes of this type have molar conductance values of *ca.* 30 ohm^{-1} cm^2 in DMF.[18] The conversion of the rhodium(II) to rhodium(I) and the reverse reaction, readily accomplished by exposure to oxygen, may be followed by changes in conductivity and visible, esr, or nmr spectroscopy; the interconversion by reaction with hydrogen and oxygen has been repeated over several cycles. The change in the visible spectra, showing good isosbestic points, is shown in Figure 2. Solutions of the rhodium(I) compound *in vacuo* give no esr signal and give a sharp nmr spectrum consistent with their formulation as a rhodium(I) tetraphenylporphyrin.

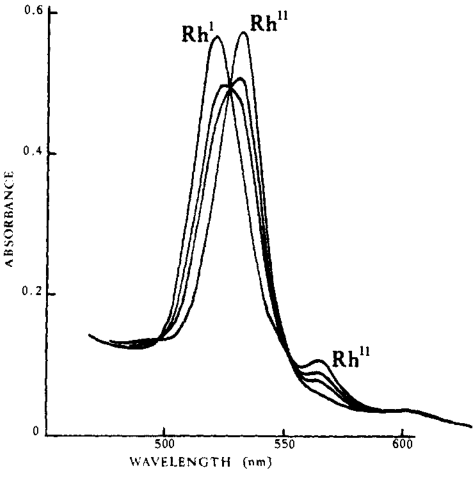
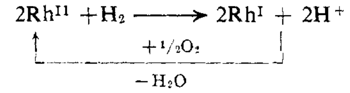


Figure 2. Visible absorption spectra of Rh^I and Rh^{II} tetraphenylporphyrin complexes in $CHCl_3$ (1-cm cell, *ca.* 5×10^{-5} *M*); intermediate spectra were recorded during oxidation of Rh^I using O_2.

The rhodium(II) compound in DMF catalyzes at ambient conditions the hydrogenation of acetylene, as well as the conversion of hydrogen–oxygen mixtures to water.



$$2Rh^{II} + H_2 \longrightarrow 2Rh^I + 2H^+ \qquad \underset{-H_2O}{\xleftarrow{+{}^1/_2O_2}}$$

No evidence has been obtained for the formation of oxygen complexes by the rhodium(II) tetraphenylporphyrin complex.

Acknowledgment. This work was supported by a grant from the National Research Council of Canada; the rhodium was loaned by Johnson Matthey Ltd. We thank Mrs. H. C. Stynes for helpful discussions and Mr. C. T. Wong for Gouy balance measurements.

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(15) A. B. Hoffman, D. M. Collins, V. W. Day, E. B. Fleischer, T. S. Srivastava, and J. L. Hoard, *J. Amer. Chem. Soc.*, **94**, 3620 (1972).

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Tris(triphenylphosphine)methyliridium(I). Synthesis, Characterization, and Thermal Decomposition

Sir:

The chemistry of transition metal alkyls continues to be a subject of widespread interest from many points of view. The synthesis,[1–5] decomposition,[3,6–8] and inorganic chemistry[4,7,8] of many transition metal alkyls

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(1) G. M. Whitesides, W. F. Fischer, J. San Filippo, Jr., R. W. Bashe, and H. O. House, *J. Amer. Chem. Soc.*, **91**, 4871 (1969), and references cited therein.

(2) E. J. Corey and G. H. Posner, *ibid.*, **90**, 5615 (1968), and references cited therein.

(3) B. Wozniak, J. D. Ruddick, and G. Wilkinson, *J. Chem. Soc. A*, 3116 (1971), and references cited therein.

(4) (a) J. Chatt and B. L. Shaw, *ibid.*, 4020, 705 (1959); (b) M. H. Chisholm and H. C. Clark, *J. Amer. Chem. Soc.*, **94**, 1532 (1972), and references cited therein.

(5) G. Yagupsky, C. K. Brown, and G. Wilkinson, *J. Chem. Soc. A*, 1392 (1970).

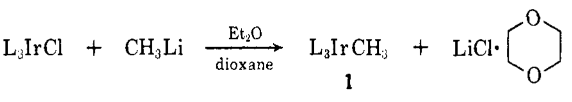
(6) G. M. Whitesides, C. P. Casey, and J. K. Krieger, *J. Amer. Chem. Soc.*, **93**, 1379 (1971), and references cited therein.

(7) G. M. Whitesides and W. J. Ehmann, *ibid.*, **92**, 5625 (1970).

(8) W. Keim, *J. Organometal. Chem.*, **14**, 179 (1968).

have been extensively explored, but there are few unique examples reported of applications of such compounds to organic synthesis. Significant among these examples are the many new syntheses involving organocopper(I) complexes.[1,2,9] Coordinatively unsaturated[10] iridium(I) or rhodium(I) alkyls (d^8 metals) may prove to be useful substrates for alkylation, as are many copper(I) alkyls (d^{10} metal), once it is possible to capitalize in a generalized way on the ability of the former metals to undergo oxidative addition[10] followed by reductive elimination[10] reactions. Despite their great synthetic potential, however, reports concerning coordinatively unsaturated alkylrhodium(I) complexes are few,[7,8] and studies involving unsaturated iridium(I) alkyls have been limited, heretofore, to the occurrence of such species as unisolated intermediates in catalytic processes[5] and not as discrete entities. We describe herein the synthesis of tris(triphenylphosphine)methyliridium(I) (L_3IrCH_3, **1**), a compound noteworthy for its susceptibility to oxidative addition which far exceeds that reported for similar alkylrhodium(I)[7,8] or alkylplatinum(II)[4a] species. We also describe the thermal decomposition of **1** as an example of an oxidative addition–reductive elimination sequence and report our observation of the formation of a hydridoiridium(III) species as an intermediate in this process.

The synthesis of L_3IrCH_3 is straightforward and is shown in eq 1. In a typical experiment, slightly more



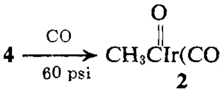
(1)

L = PPh$_3$

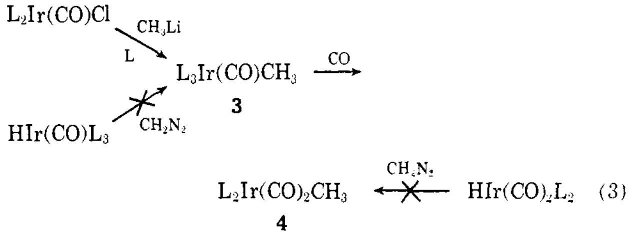
than 1 equiv of an ethereal solution of methyllithium was added to a stirred suspension of tris(triphenylphosphine) chloroiridium[11] (L_3IrCl), in ether, under an argon atmosphere at 0°. After several minutes, the color of the solution changed from orange to red. Addition of slightly more than 1 equiv of dioxane caused precipitation of lithium chloride as its dioxane adduct.[12] Excess methyllithium was destroyed by addition of several drops of methanol. The cloudy reaction mixture was clarified by centrifugation, and the deep red ethereal solution of **1** was transferred to a flask, under argon, *via* syringe. Removal of solvent, *in vacuo*, yielded the product as a bright red solid. Red, crystalline L_3IrCH_3 can be prepared by addition of pentane to a concentrated ethereal solution of the complex. The thermal stability of L_3IrCH_3 is enhanced by the presence of ether,[13] and concentrated ethereal solutions of the alkyliridium are thermally stable for several hours at 0° whereas precipitated crystals of the organometallic rapidly decompose, even at −78°. It was therefore impossible to obtain reliable elemental analysis for L_3IrCH_3.

Evidence in favor of the proposed structure for **1** is derived from the stepwise carbonylation of L_3IrCH_3 to the known[14] acetyliridium(I) derivative **2**. When a solution of L_3IrCH_3 in ether was exposed to CO (1 atm), the color of the solution immediately changed from red to yellow. Addition of ethanol yielded bright yellow, thermally stable crystals of $L_3Ir(CO)CH_3$ (**3**), 70% yield based on L_3IrCl, $\nu_{C\equiv O}$ 1945 cm^{-1}. *Anal.* Calcd for $C_{56}H_{48}OP_3Ir$: C, 65.72; H, 4.73; P, 9.10. Found: C, 64.48; H, 4.83; P, 9.00. Complex **3** was converted to the acetyliridium(I) species **2** ($\nu_{C\equiv O}$ 1980, 1925, 1620 cm^{-1}) by stirring a suspension of **3** in ethanol under 60 psi of CO (eq 2). We were able to prepare $L_3Ir(CO)CH_3$ (**3**) through reaction of methyllithium with *trans*-$L_2Ir(CO)Cl$ in the presence of excess triphenylphosphine in ethereal solution in analogous fashion to that reported[5] for synthesis of **4** from *trans*-$L_2Ir(CO)Cl$ and methyllithium in the presence of CO (eq 3). However, the yield of $L_3Ir(CO)CH_3$ prepared by this route was low, and complete separation of the product from $L_2Ir(CO)Cl$ could not be effected by crystallization techniques. We were unable to prepare $L_3Ir(CO)CH_3$ or $L_2Ir(CO)_2CH_3$ by reaction of diazomethane with the appropriate iridium hydride (eq 3).[15]

$$\underset{\mathbf{1}}{\mathrm{L_3IrCH_3}} \xrightarrow[\text{1 atm}]{\mathrm{CO}} \underset{\mathbf{3}}{\mathrm{L_3Ir(CO)CH_3}} \xrightarrow[\text{60 psi}]{\mathrm{CO}} \underset{\mathbf{4}}{\mathrm{L_2Ir(CO)_2CH_3}} + \mathrm{L}$$



$$\mathbf{4} \xrightarrow[\text{60 psi}]{\mathrm{CO}} \underset{\mathbf{2}}{\mathrm{CH_3\overset{O}{\overset{\|}{C}}Ir(CO)_2L_2}} \qquad (2)$$



(3)

The thermal decomposition of L_3IrCH_3 was also investigated. When the infrared spectrum of a Nujol mull of freshly prepared, bright red, solid L_3IrCH_3 etherate[16] was recorded over a period of 15 min at room temperature, an intense band at 2130 cm^{-1} rapidly appeared, grew slightly in intensity, and then slowly disappeared. Crystalline L_3IrCH_3 decomposed rapidly at room temperature to yield a cream-colored powder whose ir spectrum showed no band at 2130 cm^{-1} and to which structure **6** is assigned.[7,8] The ir spectrum (KBr) of **6** contains, in general, bands attributable to coordinated triphenylphosphine. A notable exception is the presence of a strong shoulder at 745 cm^{-1} indica-

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[9] The reaction of alkylcopper(I) "ate" complexes with CO to yield symmetrical ketones has been discovered (J. Schwartz, *Tetrahedron Lett.*, 2803 (1972)).

[10] J. P. Collman, *Accounts Chem. Res.*, **1**, 136 (1968); J. Halpern, *ibid.*, 3, 386 (1970).

[11] M. A. Bennett and D. L. Milner, *J. Amer. Chem. Soc.*, **91**, 6983 (1969).

[12] When dioxane was not added to the reaction mixture, poor yields of L_3IrCH_3 resulted. We are presently investigating the possibility that an equilibrium situation, $L_3IrCl + CH_3Li \rightleftarrows L_3IrCH_3 + LiCl$, which is displaced by precipitation of lithium chloride by dioxane, governs the formation of L_3IrCH_3. A similar equilibrium has been observed in alkylplatinum(II) chemistry.[4a]

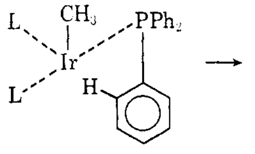
[13] The enhancement in thermal stability of L_3IrCH_3 afforded by the solvent was found to be greater in ether containing 20 *equiv* of dioxane or 20 *equiv* of THF than it was in pure ether. This increase in stability was reflected by an improved yield of $L_3Ir(CO)CH_3$ from L_3IrCH_3 which was prepared in the presence of excess dioxane or THF. These improved relative yields are 1.0 (pure ether), 1.1 (ether and 20 equiv of dioxane), and 1.6 (ether and 20 equiv of THF).

[14] J. P. Collman, F. D. Vastine, and W. R. Roper, *J. Amer. Chem. Soc.*, **90**, 2282 (1968).

[15] For the successful preparation of $CH_3Mn(CO)_5$ from diazomethane and $HMn(CO)_5$, see W. Hieber and G. Wagner, *Z. Naturforsch., B*, **12**, 478 (1957).

[16] Evacuation removal of most of the solvent from ethereal L_3IrCH_3 yielded a red amorphous solid which was stable for several minutes at room temperature. If coordinated ether was removed at −78° by continued evacuation or by washing the red solid with pentane, deep red crystalline material could be obtained. These crystals were rapidly decolorized by warming above −78°.

tive of an ortho-disubstituted benzene ring. The spectrum (4000–650 cm^{-1}) is qualitatively identical with that reported[8] for the rhodium analog of **6**. We were unable to satisfactorily purify **6** by recrystallization, and, therefore, reproducible elemental analyses were not obtained. The mass spectrum of **6** was recorded and it substantiates the designated structure for the compound. It shows important peaks (70 eV), consistent with the natural abundance ratio of ^{191}Ir:^{193}Ir of 0.63:1.00, at *m/e* (rel intensity) 978 (53, M$^+$[^{193}Ir], 976 (34, M$^+$[^{191}Ir], 977 (100, M − H), 975 (60, M − H), 715 (30), 714 (81), 713 (43), 712 (60), 711 (23), 637 (27), 636 (80), 635 (27), 634 (63), 633 (23), and 632 (23). The mass spectrum also contains a large peak at *m/e* 262 (PPh$_3$). These observations, and that of the enhanced thermal stability ot L_3IrCH_3 imparted by solution in ether, are consistent with a mechanism for thermal decomposition of L_3IrCH_3 which proceeds through the intermediary formation of the hydridoiridium(III) species **5**, as shown in eq 4. Complex **5** is analogous to those intermediates in the thermal decomposition process postulated[7,8] for L_3RhCH_3 and isolated[11] for L_3IrCl (see eq 4). It is entirely reasonable that the enhancement of thermal stability observed for L_3IrCH_3 in the presence of ether is due to coordination of a solvent molecule to iridium(I) to yield a coordinatively saturated five-coordinated species which does not readily undergo the intramolecular oxidative addition process to yield **5**. The very great reactivity ot L_3IrCH_3 compared to that observed for similar iridium(I),[11] rhodium(I),[7,8] and platinum(II)[4] species is demonstrated in that intramolecular oxidative addition occurs rapidly for L_3IrCH_3 at 0°, whereas this process occurs slowly for L_3IrCl in hot benzene, very slowly for L_3RhCH_3 at 120°, and is not reported to occur for platinum(II) alkyls.



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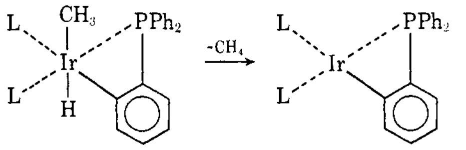

(4)

5

6

Our studies describing other oxidative addition reactions of L_3IrCH_3, as well as several uses of this complex in organic synthesis, will be reported in the near future.

Acknowledgment. The authors gratefully acknowledge support for this work given by the Petroleum Research Fund, administered by the American Chemical Society (Grant PRF-2454-GI). The authors acknowledge the generosity of Hoffmann-La Roche, Inc., in providing them with elemental analysis services. They also thank Dr. Joan S. Valentine for her helpful comments and suggestions.

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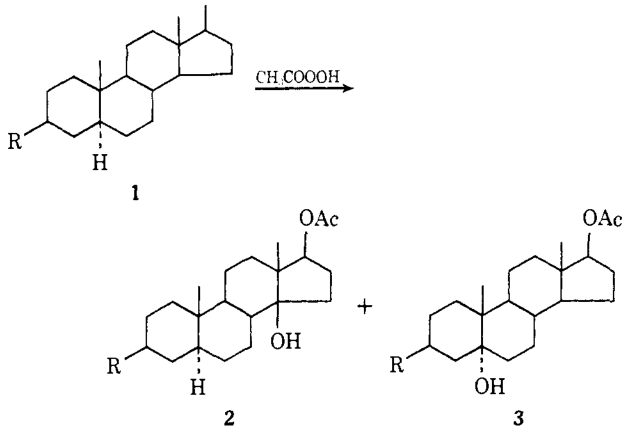
Free-Radical Hydroxylation of Steroids

Sir:

We have previously established[1] the feasibility of an attack on an unactivated tertiary carbon atom in saturated steroids substituted elsewhere by oxygenated functions. It was found that the 14α and 5β hydrogens of **1a** and **1b** were equilibratable with their epimers by bromine atoms generated photochemically *in situ* from mercuric bromide or *N*-bromosuccinimide.

We have now found that hydroxyl substitution at these unactivated centers can be accomplished by irradiation of the substrate with commercial peracetic acid.[2,3]

Thus, a 1.5% solution of androstane-3β,17β-diol diacetate (**1a**) and 8 mol equiv of peracetic acid (15% in acetic acid) in *tert*-butyl alcohol was irradiated with a high-pressure 200-W Hanovia mercury lamp using a Vycor filter. The total product was chromatographed on silica gel resulting in 20% of a 1:1 mixture of the 14β-hydroxy and 5α-hydroxy derivatives **2a** and **3a**, 50% recovered starting material, and a mixture of more polar products. Compound **2a** showed a well-defined nmr doublet for the 17α hydrogen which we have previously found to be characteristic of a 17α hydrogen of 14β steroids.[1a] The structure of **2a** was proven by correlation with a 14β-hydroxylated steroid synthesized from 14β,15β-epoxy-3β-acetoxy-5α-androstan-17-one. Results did not seem to depend strongly on the percentage of peracetic acid or the solvent. The light source could be replaced by lamps emitting at 300 mμ.



1

2

3

a, R = OAc
b, R = H

Similar treatment of 17β-acetoxy-5α-androstane (**1b**) also resulted in a 1:1 mixture of the 14β-hydroxy and 5α-hydroxy derivatives **2b** and **3b** (25% total yield).

We view this reaction as proceeding *via* hydrogen atom abstraction by methyl radicals generated photochemically from peracetic acid according to the scheme of Heywood, *et al.*[3]

It is of great interest to compare these results with those recently published by Breslow, *et al.*,[4] in which

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[1] (a) M. Gorodetsky and Y. Mazur, *J. Amer. Chem. Soc.*, **90**, 6540 (1968); (b) M. Gorodetsky, D. Kogan, and Y. Mazur, *ibid.*, **92**, 1094 (1970).

[2] Previous hydroxylation work with peracetic acid was performed only on hydrocarbons (adamantane and decalin) and employed the specially prepared anhydrous 85–100% reagent.[3]

[3] D. L. Heywood, B. Phillips, and H. A. Stansburg, Jr., *J. Org. Chem.*, **26**, 281 (1961).

[4] R. Breslow, J. A. Dale, P. Kalicky, S. Y. Liu, and W. N. Washburn, *J. Amer. Chem. Soc.*, **94**, 3276 (1972).