ation of chemical shift with pH and employing as model compounds actinamine, *N,N'*-diacetylactinamine, dihydrospectinomycin, and *N,N'*-diacetyldihydrospectinomycin.[15] Our assignments (Table I) agree with those of Grutzner except for C-1, C-3, C-4, and C-6. In addition, we assign the signals at 31.8 and 31.3 ppm to the 1-*N*- and 3-*N*-methyl carbons, respectively, and differentiate between C-2' and C-3' while Grutzner did not distinguish between these atoms.

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R. M. Stroshane,[17] M. Taniguchi, K. L. Rinehart, Jr.*
Roger Adams Laboratory, University of Illinois
Urbana, Illinois 61801

J. P. Rolls, W. J. Haak, B. A. Ruff
The Upjohn Company
Kalamazoo, Michigan 49001

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Electrochemical Reduction and Bonding in the O_2, S_2, and Se_2 Adducts of $[Ir\{(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2\}_2]^+$

Sir:

We wish to report here novel electrochemical behavior and its bonding implications for the series $[Ir(dppe)_2X_2]^+$ (dppe = $Ph_2PCH_2CH_2PPh_2$; $X_2 = O_2$, S_2, and Se_2).[1-4] This study reveals for the first time the dissociation of $X_2\cdot^-$ consequent to the addition of one electron to the antibonding orbital of the π-component of the widely accepted Dewar–Chatt–Duncanson model[5] for MX_2 bonding; it also provides a means of assessing the π-back-bonding interaction between the metal and the X_2 group.

Cyclic voltammograms (100 mV/s) of degassed 10^{-3} M solutions of $[Ir(dppe)_2X_2]^+$ and $[Ir(dppe)_2]^+$ in CH_3CN (using 0.1 M $(n\text{-}C_4H_9)_4N^+ClO_4^-$ as supporting electrolyte, Ag/0.01 *M* $AgNO_3$ as reference electrode and a hanging mercury drop as working electrode) are shown in Figure 1. $Ir(dppe)_2^+$ has one quasi-reversible reduction wave at −2.05 V. The O_2, S_2, and Se_2 adducts each have two reduction waves: the first wave (A) is irreversible and progresses to more negative potential, viz., −1.64, −1.75, and −1.95 V, along the sequence Se_2, S_2, O_2 whereas the second wave (B) is quasi-reversible with potential (−2.05 V) and shape resembling that of the $Ir(dppe)_2^+$ species. At slow scan rates (10 mV/s) the cyclic voltammogram of $Ir(dppe)_2^+$ has no anodic peak. In the 100 mV/s scan $i_p^c/i_p^a \approx 2$ and the peak separation is 45 mV, while in a 200 mV/s scan $i_p^c/i_p^a \approx 1.5$ and the peak separation is 52 mV. A one-electron reversible charge transfer has $i_p^c/i_p^a = 1$ and a peak separation of 59 mV.

To clarify the nature of the reduction waves, we carried out extensive controlled potential coulometry studies on these complexes. Except for the S_2 adduct, wave A corresponds to a one (0.9–1.1) electron reduction whereas wave B corresponds to a 1.7–1.8 electron reduction. The coulometric *n* values for $Ir(dppe)_2S_2^+$ are 1.3 and 0.4 for waves A and B, respectively. We also observed that controlled potential electrolysis at potentials intermediate between waves A and B of $Ir(dppe)_2X_2^+$ produced a solution with color and cyclic voltammogram characteristic of $Ir(dppe)_2^+$. In the case of the O_2 complex, the cyclic voltammogram of this solution also showed an oxidation wave at −1.03 V, analogous to the wave found in a freshly prepared solution of authentic $O_2\cdot^-$. In all cases, further reduction at a potential more negative than wave B (i.e., −2.05 V) produced an orange precipitate identical with that obtained by similar reduction of the $Ir(dppe)_2^+$ species. The orange precipitate was characterized by elemental analysis-($Ir(dppe)_2H$), ^1H NMR in $CDCl_3$ (a 1:4:6:4:1 quintet at τ 30.04 with $J_{P\text{-}H}$ = 12 Hz), and ir (a sharp Ir-H stretching mode at 2015 cm^{-1}). A single-crystal x-ray structure determination[6] revealed a trigonal-bipyramidal-like structure (I) with the hydride (not located) presumably situated at the axial position.[7]

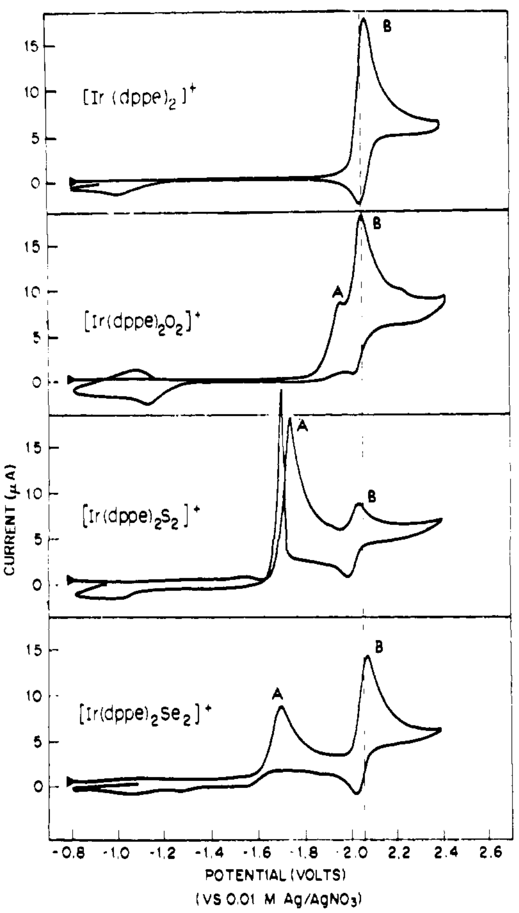
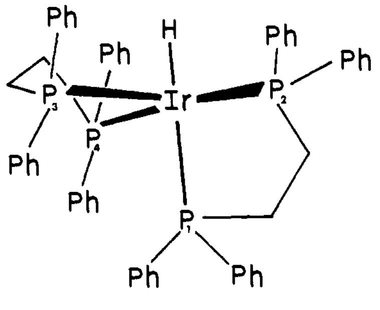


Figure 1. Cyclic voltammograms of 10^{-3} M $[Ir(dppe)_2]^+$ and $[Ir(dppe)_2X_2]^+$ ($X_2 = O_2$, S_2, and Se_2) in 0.10 M $(n\text{-}C_4H_9)_4N^+ClO_4^-$ in CH_3CN: scan rate, 100 mV/s; scan initiated at arrowhead. The sharp reduction peak at −1.65 V on the reverse (anodic) scan for the S_2 adduct disappears when a Pt-bead is used as the working electrode, or when the scan rate is greater than 500 mV/s with a hanging mercury drop electrode. Its origin is at present not understood.



I

To trace the source of the hydride, controlled-potential coulometry was repeated using CD_3CN as solvent. The orange precipitate now showed a loss of about 80% in the intensity of its Ir-H stretching band at 2015 cm^{-1}, and a new band appeared at 1445 cm^{-1}, as expected for the Ir-D stretch. This suggests that about 80% of the hydride comes from the solvent, with the remaining 20% most likely from the ortho-phenyl hydrogen of the dppe ligand or the supporting electrolyte.[9]

Based on the above observations, we propose the following mechanism for the electrolytic reduction of these complexes:

$$[\mathrm{Ir(dppe)_2X_2}]^+ \xrightarrow[\mathrm{A}]{1\,\mathrm{e}}$$

$$\mathrm{X_2 = O_2, S_2, Se_2}$$

$$\begin{tikzcd}
{[\mathrm{Ir(dppe)_2X_2}]^0} \arrow[d, "k_\mathrm{d}"] & & \\
{[\mathrm{Ir(dppe)_2}]^+} \arrow[r, "1\,\mathrm{e}", "\mathrm{B}"'] & {[\mathrm{Ir(dppe)_2}]^0} \arrow[d, "k_\mathrm{H}"'] & \begin{matrix} 0.8\mathrm{CH_3CN} \\ 0.2\mathrm{RH} \end{matrix} \\
+ & \mathrm{Ir(dppe)_2H} & \\
\mathrm{X_2\cdot^-} & + & \\
& 0.8\mathrm{CH_2CN\cdot} \arrow[r, "0.8\,\mathrm{e}", "\mathrm{B}"'] & \mathrm{CH_2CN\cdot^-} \\
& + & \\
& 0.2\mathrm{R\cdot} &
\end{tikzcd}$$

That is, the first reduction wave (A) represents addition of one electron to an orbital which is highly antibonding between the metal and the X_2 group; the latter immediately and irreversibly dissociates off as the $X_2\cdot^-$ radical anion. We thus get back unadducted $\mathrm{Ir(dppe)_2}^+$ which is further reduced at wave B by one electron to form a highly reactive Ir(0) d^9 complex; the latter then abstracts a hydrogen atom from the environment to form orange $\mathrm{Ir(dppe)_2H}$ precipitate. Since approximately 80% of the hydride comes from CH_3CN it is plausible to assume that the $CH_2CN\cdot$ radical formed can be further reduced to the corresponding anion at wave B, thus accounting for the coulometric $n = 1.7$–1.8 for that wave. It is, however, also possible that both the $CH_2CN\cdot$ and $R\cdot$ radicals are reduced at wave B, but that a competing coupling reaction decreases n from 2 to ~1.8. The anomalous n values obtained for the S_2 complex are presumably due to interference by $S_2\cdot^-$ or its reaction products.[10]

The two most important implications of this research are: (1) The lowest unoccupied molecular orbital, to which one electron is added at wave A, must be strongly antibonding between the metal and the X_2 group. In terms of the Dewar-Chatt model the orbital involved arises from interaction between a metal d orbital and the π^* orbital of X_2 which lies in the MX_2 plane. (2) The progression of the first reduction wave (A) to more negative potential for $X_2 = Se_2 \rightarrow S_2 \rightarrow O_2$ is taken to indicate that this π-back-bonding interaction enhances in the same direction, thereby causing stepwise destabilization of the lowest unoccupied molecular orbital along this sequence. These two conclusions are supported by molecular orbital calculations on the model complexes $\mathrm{Rh(PH_3)_4X_2}^+$ using Fenske's method.[12] Details will be presented elsewhere.

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(6) $\mathrm{Ir(dppe)_2H}$: monoclinic $P2_1/n$; $a = 21.260$ (5), $b = 20.809$ (3), $c = 10.107$ (3) Å; $\beta = 91.44$ (2)°; $V = 4470$ (2) Å^3; and $Z = 4$. Anisotropic least-squares refinement gave $R_1 = 3.65\%$ and $R_2 = 4.15\%$ for 3452 independent reflections. The important bond lengths (Å) and angles (deg) are: Ir–P_1 2.278 (2), Ir–P_2 2.245 (2), Ir–P_3 2.279 (2), Ir–P_4 2.271 (2); P_1–Ir–P_2 83.99 (9), P_3–Ir–P_4 87.64 (9), P_1–Ir–P_3 106.14 (9), P_1–Ir–P_4 107.02 (9), P_2–Ir–P_3 125.07 (9), P_2–Ir–P_4 141.89 (9).

(7) This complex is identical with a known compound[8] in color, stoichiometry, and ν(Ir–H) frequency, but the high-field proton NMR spectrum observed by us differs from the previously reported spectrum.

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(10) In contrast to our proposal that the electrochemical reduction of $\mathrm{Ir(dppe)_2}^+$ takes place by a one-electron transfer followed by hydrogen abstraction, a previous study of this compound[11] concluded that a two-electron transfer followed by proton abstraction is involved. This, however, is clearly inconsistent with the observed cathodic-anodic peak separation and scan rate dependence of the cyclic voltammograms, and also with the fact that deuteration occurs with CD_3CN but not D_2O.

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Boon-Keng Teo, A. P. Ginsberg*
Bell Laboratories
Murray Hill, New Jersey 07974

J. C. Calabrese
Department of Chemistry
University of Wisconsin
Madison, Wisconsin 53706

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A Remarkable Epoxide Opening. An Expeditious Synthesis of Vernolepin and Vernomenin

Sir:

The novel structural and stereochemical features of the sesquiterpenes vernolepin (**19**) and vernomenin (**20**)[1,2] have stimulated a great deal of synthetic activity.[3,4] The tumor inhibitory properties which have been ascribed to these compounds[5] (albeit only in preliminary screening experiments which lack clear clinical implications) augment interest in their assemblage. Extensive studies have recently culminated in the first total synthesis of **21** and **22** by Grieco and co-workers.[6] As a consequence of the demonstration of the feasibility of bis α-methylenation on synthetic precursors **17** and **18**, these "*bis-nor*" compounds may now be regarded as terminal objectives in a total synthesis exercise. Below we report a short stereospecific synthesis of **17** and **18**.

A Diels-Alder strategy was employed to ensure the required $5\alpha,10\alpha$ (steroid numbering) fusion (**1** + **2** → **3**). The angular function at position 10 induces the proper α-oxygen asymmetry at C_8 (**4** → **5**). The α-hydroxyl group at C_8 is used, in a Henbest fashion,[7] to introduce $6\alpha,7\alpha$-oxido stereochemistry (**8** → **9**). Eventually, this epoxide is opened by dilithioacetate to give the necessary $6\alpha,7\beta$ substituents. A key feature of the synthesis is the use of a spiro orthoester linkage which simultaneously protects the A ring lactone while exerting a strong orientational influence on the direction of epoxide opening (**15a** → **16a**). The synthesis is described below.

Diels-Alder reaction of methyl 2,5-dihydrobenzoate (**1**)[8] with the diene, **2**[9] (4 equiv of **2**; mesitylene; reflux; 48 h), gives a 50% yield (39% efficiency)[10] of dienone **3**.[11] Although this yield is not impressive, it should be noted that cyclohexenecarboxylates are notoriously unreactive as dienophiles.[9b]

Ester **3** is saponified in quantitative yield to give acid **4**.[11] Iodolactonization of **4** ($\mathrm{NaHCO_3}$–$\mathrm{KI_3}$–$\mathrm{H_2O}$; room temperature; 48 h) affords **5**[11] (88% yield). Reaction of **5** with diazabicycloundecene (DBU) provides dienonelactone **6** in 87% yield. This compound exhibited strong resistance to attack by peracids.[12] However, upon reaction with excess p-nitroperbenzoic acid for 10 days, a 33% yield of the undesired $6\beta,7\beta$-isomer, **7**,[11] was obtained. This reflects the deactivation of the α-face of the molecule by the α-lactone bridge.

The epoxide stereochemistry was controlled as follows. Reaction of lactone **6** with aqueous sodium hydroxide (THF, room temperature 5 h) gave a quantitative yield of hydroxy acid **8**.[11] In sharp contrast to the case of **6**, **8** reacts with 1.1 equiv of m-chloroperbenzoic acid (MCPBA; room temperature; 10 h) to give an epoxy acid, mp 117–118°, which, upon treatment with sodium acetate-acetic anhydride (80°; 3 h) gives **9**[11] (85% from **6**). The stereochemical and rate differ-