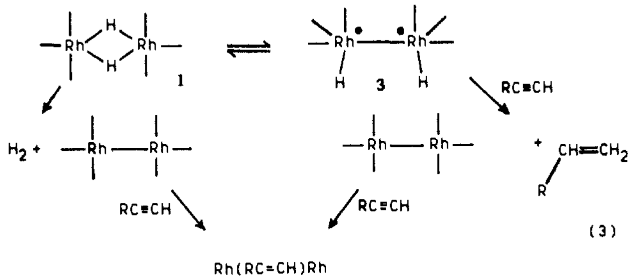
cumene, no styrene containing olefinic protons is observed.

The results of our experiments lead us to the inescapable conclusion that the radical pair responsible for CIDNP in the reaction of **1** with alkynes must be a metal-centered biradical (MCBR). The major polarizations we see only occur in the hydrogens originally on **1**. For a pure multiplet effect, Δg of the radical pair must be zero, but a radical pair based on styrenyl radicals is totally inconsistent with experiment. We therefore propose that **1** rapidly and reversibly forms a biradical isomer **3** which undergoes singlet–triplet mixing and spin-selective reaction to produce CIDNP. The "singlet" reaction channel of **3** is recombination to **1**, whereas the escape or "triplet" channel corresponds to reaction with $RC\equiv CH$, as shown in eq 3.[13] Application of Kaptein's rule for multiplet effects based on this analysis leads to the prediction of A/E polarization of the geminal and trans resonances in accord with our observations.[14] That the addition of H_2 to the alkyne occurs with predominantly cis stereochemistry and very little or no net effect indicates that the biradical **3** transfers its H atoms to $RC\equiv CH$ in an essentially concerted manner.



(3)

To our knowledge this is the first example of CIDNP based on a metal-centered biradical. Our CIDNP results may be compared with those of Closs and Kaptein for organic biradicals in which singlet–triplet mixing occurs by either a spin-sorting mechanism as is seen in the present study or by T_-–S mixing which leads to emission effects exclusively.[15] The latter is dominant when the exchange integral J, which reflects the singlet–triplet splitting, is large and comparable to the Zeeman splitting; our results suggest that in the case of **3**, J is relatively small. Further experimental and theoretical work on biradicals such as **3** is needed.

While the present study is the first to recognize the MCBR for producing CIDNP, one other report involving a polynuclear transition-metal organometallic compound shows similar effects.[16] Specifically, Bergman et al. find multiplet effects in the hydrogenolysis of $Co_3(CO)_9(\mu_3\text{-}CCH_2\text{-}t\text{-}Bu)$ to give $t\text{-}BuCHCH_2$ with polarization only in the protons originating from H_2.[16] We think that that reaction may also proceed via a metal-centered biradical, and we suggest that MCBR mechanisms which are difficult to detect may occur more commonly in reactions involving polynuclear transition-metal hydrides.

Acknowledgment. We thank the Office of Naval Research and the National Science Foundation (CHE 83-08064) for support of this work and the Johnson Matthey Co., Inc., for a generous loan of rhodium salts. We also acknowledge helpful and informative discussions with Prof. N. J. Turro, Dr. C. Doubleday, Prof. R. G. Lawler, Prof. G. L. Closs, Prof. R. G. Bergman, and Dr. H. Bryndza.

Registry No. 1, 91759-40-9; **2**, 80846-11-3; $PhC\equiv CH$, 536-74-3; $MeC\equiv CH$, 74-99-7; $t\text{-}BuC\equiv CH$, 917-92-0; $EtC\equiv CH$, 107-00-6; $HC\equiv CCOOMe$, 922-67-8; $HC\equiv CCH_2OH$, 107-19-7; $CH_3C\equiv CCH_2OH$, 764-01-2.

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(13) Complex **1** undergoes facile loss of H_2 in the absence of other reagents.[5] This loss of H_2, seen in the present study when reaction 2 is done under N_2 with lower resultant yields of styrene, is not necessary to explain the observed multiplet effects. However, in some experiments, significant enhancement of H_2 absorption is detected. This result cannot be explained by **3** and suggests the possibility of a second metal-centered biradical such as one with both H's on a single Rh center prior to H_2 reductive elimination. This observation is under continuing study.

(14) The A/E phase of the multiplet effect is determined from Kaptein's rule[11] assuming a singlet precursor, escape or triplet products, a positive spin–spin coupling constant, and the fact that the coupled nuclei are on different radical centers of the MCBR.

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Hydrido Methylidene, Hydrido Vinylidene, Hydrido Oxo, and Hydrido Formaldehyde Derivatives of Bis(pentamethylcyclopentadienyl)tantalum

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Transition-metal complexes of the general class $L_nM(H)(=X)$ ($X = CH_2$; $C = CH_2$, O) are of interest as models for reactive intermediates in a variety of catalytic processes. Hydrido alkylidene complexes, generated by a 1,2-hydrogen shift from metal alkyls, have been postulated to play an important role in the metathesis and polymerization of olefins,[1] while surface-bound vinylidene species have been detected[2] and recently proposed to account for linear/branched hydrocarbon distributions in Fischer–Tropsch synthesis.[3] The third member of the class described here, $L_nM(H)(=O)$, is of fundamental importance in reactions involving H_2O, O_2, or peroxides. Although an example of an oxo hydride has not previously been reported, several oxo alkyl species have been characterized recently.[4]

We have described the preparation of a number of permethyltantalocene derivatives and commented on the remarkable stability conferred by two pentamethylcyclopentadienyl ligands.[5] This important facet and a general reluctance for permethylmetallocene derivatives to undergo oligomerization processes have allowed us to prepare and investigate the reaction chemistry of a number of monomeric hydrido derivatives of general formula,

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$Cp^*_2Ta(H)({=}X)$ [$Cp^* = \eta^5\text{-}C_5Me_5$; X = CH_2 (**1**), $C{=}CH_2$ (**2**), O (**3**)]. We have also isolated an η^2-formaldehyde adduct $Cp^*_2Ta(H)(\eta^2\text{-}CH_2O)$ (**4**). Such species continue to attract interest as models for possible intermediates in CO hydrogenation,[6] and we describe herein a novel C–O bond cleavage reaction at elevated temperatures to afford the oxo alkyl derivative, $Cp^*_2Ta(CH_3)({=}O)$.

The reaction of $Cp^*_2TaCl_2$ with 2 equiv of methyllithium in diethyl ether proceeds smoothly at room temperature over a period of 36 h to afford $Cp^*_2Ta(H)({=}CH_2)$ (**1**) in 80% yield (eq 1).

$$Cp^*_2TaCl_2 \xrightarrow[Et_2O]{2CH_3Li} \underset{\mathbf{1}}{Cp^*_2Ta(H)({=}CH_2)} \qquad (1)$$

At room temperature **1** shows a characteristic low-field shift for the methylidene carbon at δ 239.5 (t, J = 127 Hz)[7] and singlets in the ^1H NMR spectrum at δ 10.17 and 1.75 attributable to the methylidene hydrogens and metal hydride, respectively. As the temperature is raised these proton signals broaden[8] due to rapid exchange of hydrogens between methylidene and metal hydride sites, according to the 1,2-hydrogen shift equilibrium shown in eq 2. Moreover, magnetization transfer [$Ta(H)({=}\mathit{CH_2}) \rightleftarrows$

$$\underset{\mathbf{1}}{Cp^*_2Ta(H)({=}CH_2)} \rightleftarrows$$

$$[Cp_2^*TaCH_3] \xrightleftharpoons[h\nu,\,-CO]{CO} \underset{\mathbf{5}}{Cp^*_2Ta(CH_3)(CO)} \qquad (2)$$

$Ta(\mathit{H})({=}CH_2)$] is observed at 25 °C, and the 16-electron tantalum methyl complex may be trapped under 1 atm of carbon monoxide to yield $Cp^*_2Ta(CH_3)(CO)$ (**5**).

The reaction of $Cp^*_2TaCl_2$ and vinylmagnesium bromide in THF gives the neutral hydrido vinylidene species, $Cp^*_2Ta(H)({=}C{=}CH_2)$ (**2**), in 75% yield (eq 3). NMR data [^1H NMR:

$$Cp^*_2TaCl_2 \xrightarrow[THF]{2CH_2{=}CHMgBr} \underset{\mathbf{2}}{Cp^*_2Ta(H)({=}C{=}CH_2)} \qquad (3)$$

$(\eta^5\text{-}C_5(\mathit{CH_3})_5)_2Ta(H)(C{=}CH_2)$ δ 1.90 (s); $Cp^*_2Ta(\mathit{H})(C{=}CH_2)$ δ –0.03 (br s); $Cp^*_2Ta(H)(C{=}\mathit{CH_2})$ δ 6.05 (dd, $^2J_{HH}$ = 12.8, $^4J_{HH}$ = 2.7 Hz) and 6.20 (dd, $^2J_{HH}$ = 12.8, $^2J_{HH}$ = 2.7 Hz). ^{13}C NMR: $Cp^*_2Ta(H)(\mathit{C}{=}\mathit{CH_2})$ δ 354 (C_α) and 109 (C_β) ($^1J_{CH}$ = 157 Hz)[9]] support a structure with all atoms of the [$Ta(H)(C{=}CH_2)$] moiety in the same plane, as expected for maximal overlap of the frontier orbitals of [Cp^*_2TaH] and [$C{=}CH_2$]. Reaction with carbon monoxide (1 atm) at 60 °C affords green $Cp^*_2Ta(CH{=}CH_2)(CO)$ (**6**) quantitatively. Irradiation of **6** with a medium-pressure mercury lamp at room temperature (even in the presence of excess CO) cleanly regenerates **2** (eq 4). Similarly, photolysis

$$\underset{\mathbf{2}}{Cp^*_2TaH({=}C{=}CH_2)} \rightleftarrows [Cp^*Ta(CH{=}CH_2)] \xrightleftharpoons[h\nu,\,-CO]{CO,\ 60\ °C} \underset{\mathbf{6}}{Cp^*_2Ta(CH{=}CH_2)(CO)} \qquad (4)$$

of **5** under dinitrogen flush regenerates **1** (eq 2). Thus, both **1** and **2** undergo reversible α-hydrogen shifts. Complex **1** represents the first isolated example of a compound containing the elusive hydrido methylidene moiety. The equilibrium between ethenyl and hydrido vinylidene (eq 4) bears similarity to the equilibration of alkylidene and alkylidyne hydrido complexes reported by Schrock and co-workers.[10]

The reaction of **1** with the methylidenetrimethylphosphorane, $CH_2{=}PMe_3$ cleanly affords $Cp^*_2Ta(CH_3)({=}CH_2)$ (**7**). Since **1**-d_3 and $CH_2{=}PMe_3$ give rise to $Cp^*_2Ta(CD_3)({=}CH_2)$ exclusively, it appears that the ylide (like CO in eq 2) serves to trap the 16-electron [$Cp^*_2TaCH_3$], according to eq 5.

$$\underset{\mathbf{1}}{Cp^*_2Ta(H)({=}CH_2)} \rightleftarrows [Cp^*_2TaCH_3] \xrightarrow{CH_2PMe_3}$$
$$[Cp^*_2Ta(CH_3)(CH_2PMe_3)] \xrightarrow{-PMe_3} \underset{\mathbf{7}}{Cp^*_2Ta(CH_3)({=}CH_2)} \qquad (5)$$

On treatment with 1 equiv of water, **1** and **2** liberate methane and ethylene, respectively, to give the same product, $Cp^*_2TaH({=}O)$ (**3**) according to eq 6. Presumably, **3** arises by an intra-

$$Cp^*_2Ta(H)({=}X) \xrightarrow[-H_2X]{H_2O} [Cp^*_2TaOH] \rightarrow$$
$$\underset{\mathbf{3}}{[Cp^*_2Ta(H)({=}O)]} \quad (X = CH_2,\ C{=}CH_2) \qquad (6)$$

molecular O–H α-H elimination from the 16-electron intermediate [Cp^*_2TaOH], since **1** and D_2O yield only $Cp^*_2Ta(D)({=}O)$ and CH_3D.

On reaction with methanol, **1** and **2** yield an usual hydrido η^2-formaldehyde complex, $Cp^*_2Ta(H)(\eta^2\text{-}CH_2O)$ (**4**), which may also be prepared by stirring a mixture of $Cp^*_2TaCl_2$ and sodium methoxide over sodium amalgam. Complex **4** is believed to form by an intramolecular β-hydrogen elimination from an intermediate 16-electron methoxy species (eq 7). In agreement, $Cp^*_2Ta(D)(\eta^2\text{-}CD_2O)$ is the only product observed on reaction of

$$Cp^*_2Ta(H)({=}X) \xrightarrow[-H_2X]{CH_3OH} [Cp^*_2TaOCH_3] \rightleftarrows$$
$$\underset{\mathbf{4}}{[Cp^*_2Ta(H)(\eta^2\text{-}CH_2O)]} \quad (X = CH_2,\ C{=}CH_2) \qquad (7)$$

$Cp^*_2TaCl_2$ with Na/Hg and $NaOCD_3$. Moreover, the methoxide complexes, $Cp^*_2Ta(OMe)(CO)$ (**8**) and $Cp^*_2Ta(OMe)(CNMe)$ (**9**), are generated rapidly upon treatment of **4** with carbon monoxide or methylisocyanide, respectively (eq 8), suggesting **4** and [$Cp^*_2TaOCH_3$] are in rapid equilibrium.

$$\underset{\mathbf{4}}{Cp^*_2Ta(H)(\eta^2\text{-}CH_2O)} \rightleftarrows [Cp^*_2TaOCH_3] \xrightarrow{L}$$
$$Cp^*_2Ta(L)OCH_3 \quad (L = CO,\ \mathbf{8};\ CNCH_3,\ \mathbf{9}) \qquad (8)$$

A related compound, $W(PMe_3)_4H_2(\eta^2\text{-}CH_2O)$, recently reported by Green and co-workers,[11] releases methanol when heated at 60 °C under dihydrogen (15 atm). In contrast, thermolysis of **4** at 140 °C even in the presence of dihydrogen, leads to the new oxo species, $Cp^*_2Ta(CH_3)({=}O)$ (**10**), arising from a novel C–O bond cleavage reaction. Conversion of **4** to **10** (eq 9) follows

$$\begin{tikzcd}
\underset{\mathbf{4}}{Cp^*_2TaH(\eta^2\text{-}CH_2O)} \arrow[r, shift left, "k_1"] \arrow[drr, bend right] & {[Cp^*_2TaOCH_3]} \arrow[l, shift left, "k_{-1}"] \arrow[r, "k_2", "140\ °C"'] & {} \\
& & \underset{\mathbf{10}}{Cp^*_2TaCH_3({=}O)} \quad (9)
\end{tikzcd}$$

first-order kinetics [$k_1k_2/k_{-1} = k_{obsd}$ (140 °C) = 3.03 (3) × 10^{-6} s^{-1}; ΔG^* (140 °C) = 34.9 (2) kcal/mol]. The stepwise process shown in eq 9, rather than C–O bond breakage in concert with C–H bond formation, is in much better accord with the inverse kinetic deuterium isotope effect (k_H/k_D = 0.46(3), 140 °C) observed when $Cp^*_2Ta(D)(OCD_2)$ is thermolyzed, since a shift in the preequilbrium toward [$Cp^*_2TaOCY_3$, Y = H, D] is expected for **4**-d_3.

The structures of complexes of the type $Cp^*_2Ta(H)({=}X)$, together with the mechanisms and thermochemistry attending their formation and rearrangement, are presently under investigation.

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Supplementary Material Available: Tables of spectral (^1H NMR, ^{13}C NMR, IR, mass spectrum) and microanalytical data (4 pages). Ordering information is given on any current masthead page.

Solvent Control of Oxidation State Distribution and Electronic Delocalization in an Osmium-Ruthenium, Mixed-Metal Dimer

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In mixed-valence dimers the position and extent of delocalization of the odd electron depends on the metals and on the bridging and nonbridging ligands.[1] We report here the preparation of the mixed-metal dimer $[(bpy)_2(Cl)Os^{II}(pz)Ru^{II}(NH_3)_5]^{3+}$ (bpy is 2,2′-bipyridine; pz is pyrazine) in which the metal–ligand combinations at the two sites lead to redox potentials for the $Os^{III/II}$ and $Ru^{III/II}$ couples which are nearly of the same magnitude.[2,3] However, because of a considerable difference in the sensitivity of the potentials of the two couples to solvent,[4] we have been able to demonstrate that in the mixed-valence form of the dimer, intramolecular electron transfer can be induced by changes in the solvent. Perhaps more interestingly, we also find that variations in solvent appear to affect the extent of delocalization of the odd electron.

In acetonitrile at $\mu = 0.1$ M, reversible $E_{1/2}$ values (cyclic voltammetry) for the two metal-based redox couples in the dimer occur at +0.38 and +0.01 V vs. ferricinium/ferrocene as an internal reference (+0.72 and +0.35 vs. the saturated sodium calomel electrode).

$$M^{III}(L)M'^{III} + e^- \rightarrow M^{II}(L)M'^{III};\quad E_{1/2}(1) \qquad (1)$$

$$M^{II}(L)M'^{III} + e^- \rightarrow M^{II}(L)M'^{II};\quad E_{1/2}(2) \qquad (2)$$

The large potential difference between the III,III/II,III and II,III/II,II couples, $E_{1/2}(1) - E_{1/2}(2)$, arises chiefly from electrostatic and electronic coupling effects.[1,3] One-electron oxidation gives the mixed oxidation state dimer $M^{II}(L)M'^{III}$. From the UV–visible spectra of the mixed oxidation state dimer, the reduced dimer, and the related monomers (Figure 1) the oxidation state distribution within the dimer in nitromethane is $[(bpy)_2(Cl)Os^{III}(pz)Ru^{II}(NH_3)_5]^{4+}$ and in dimethylformamide it is $[(bpy)_2(Cl)Os^{II}(pz)Ru^{III}(NH_3)_5]^{4+}$. On going from the monomer to the dimer in nitromethane, the shift in the $d\pi[Ru^{II}(NH_3)_5] \rightarrow \pi^*(pz)$ transition from 436 to 534 nm is expected because of stabilization of $\pi^*(pz)$ by binding at the remote nitrogen of the ligand bridge.[4a,5] In dimethylformamide, the multiple $d\pi(Os^{II}) \rightarrow \pi^*(bpy)$ transitions associated with Os(II) appear and the intense band at 720 nm arises from a $d\pi(Os^{II}) \rightarrow \pi^*(pz)$ transition. Also noteworthy is the loss of the highest $d\pi \rightarrow \pi^*$ transition (420 nm) upon dimer formation; this appears to be a general property of pyrazine-bridged Os(II) dimers.

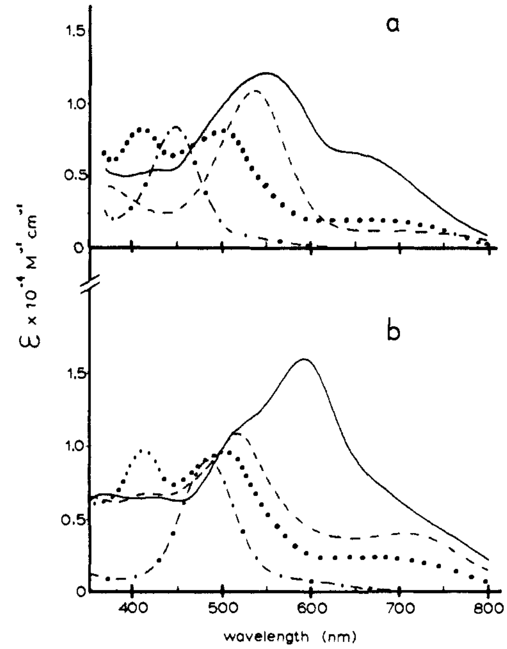

Figure 1. UV–visible absorption spectra in (a) nitromethane and (b) dimethylformamide, for $[Ru^{II}(NH_3)_5(pz)]^{2+}$ (-·-), $[(bpy)_2(Cl)Os^{II}(pz)]^+$ (···), $[(bpy)_2(Cl)Os(pz)Ru(NH_3)_5]^{4+}$ (- - -), and $[(bpy)_2(Cl)Os(pz)Ru(NH_3)_5]^{3+}$ (—).

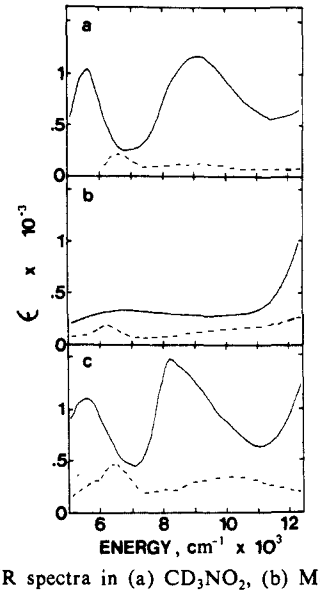

Figure 2. Near-IR spectra in (a) CD_3NO_2, (b) Me_2SO-d_6, and (c) CD_3CN, for $[(bpy)_2(Cl)Os(pz)Ru(NH_3)_5]^{4+}$ (—) and $[(bpy)_2(Cl)Os^{III}(pz)Ru^{III}(NH_3)_5]^{5+}$ (- - -).

The equilibrium between oxidation state isomers in reaction 3 can be perturbed by variations in the solvent. Spectral studies

$$[(bpy)_2(Cl)Os^{III}(pz)Ru^{II}(NH_3)_5]^{4+} \rightleftharpoons [(bpy)_2(Cl)Os^{II}(pz)Ru^{III}(NH_3)_5]^{4+} \qquad (3)$$

show, for example, that the addition of Me_2SO to CH_3NO_2 so-

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(2) The salt $[(bpy)_2(Cl)Os(pz)Ru(NH_3)_5](PF_6)_3$ was prepared by using the procedure described for the analogous Ru–Ru complex (Callahan, R. W.; Brown, G. M.; Meyer, T. J. *Inorg. Chem.* **1975**, *14*, 1443). Equimolar amounts of the solids $[(bpy)_2(Cl)Os(pz)](PF_6)$ and $[Ru(NH_3)_5(OH_2)](PF_6)_2$ were added to a deaerated 50-mL Erlenmeyer flask. Deaerated acetone was added by syringe and the mixture was stirred in the absence of light under a blanket of Ar for 1 h. The dimeric PF_6^- salt was precipitated by adding the reaction mixture dropwise into 100 mL of stirring dichloromethane. The resulting solid was collected and purified by reprecipitation from acetone/ether followed by stirring in dichloromethane to remove monomeric impurities. Anal. Calcd for $[(bpy)_2(Cl)Os(pz)Ru(NH_3)_5](PF_6)_3 \cdot 2H_2O$: C, 22.6%; H, 3.09; N, 12.08. Found: C, 20.43; H, 3.04; N, 12.08. The 4+ and 5+ dimers were prepared in situ by using Br_2 as oxidant.

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