Irradiation of the sulfides (**4–6**) isolated in oxygen matrices at 13 K gave new species, adducts **7**, **8**, and **9**, respectively, with intense IR bands at 997, 997, and 1034 cm^{-1}, respectively (Figure 2-1a∼3a). Each product behaves as a single chemical entity (i.e., the IR bands appear and disappear simultaneously at the initial stage of irradiation). Subsequent annealing[19] (at temperatures up to 40 K) did not change the IR absorption.[20] These intense bands may result from the characteristic S–O stretching mode and are consistent with the calculated value (1019 cm^{-1})[21] for a persulfoxide.[3h] It is significant that these stretching frequencies are very close to the S–O frequency (ca. 1050 cm^{-1}) in normal sulfoxide compounds. Isotopic labeling experiments show that the IR bands for **7–9** shift by 19 cm^{-1} to lower wavenumber with $^{18}O_2$ (95% doubly labeled).[23] These shifts are similar to the 28 cm^{-1} decrease in stretching frequency observed in going from $PhS(^{16}O)Me$ to $PhS(^{18}O)Me$.[24] The absence of a band at 700–900 cm^{-1} ion the IR spectra, which can be assigned to the S–O single bond stretching vibration,[26] may eliminate diradical **2** as a possible intermediate. We can conclude that these bands derive from the S–O stretching vibration in the persulfoxide **1**.

We also generated the sulfide–oxygen adducts in matrices with ^{16}O–^{18}O[27] to show which of the intermediates **1** and **3** participates in the oxidation.[28] Figure 2 shows the IR spectra in the region 1040–960 cm^{-1} from three experiments in which different isotopic mixtures of O_2 were used. In the ^{16}O–^{18}O adduct, S–O stretching vibration bands were split into two additional absorption bands.[29] Such splitting for the mixed isotope indicates that two oxygen atoms are not equivalent in the intermediate and therefore rules out the dioxathiirane structure **3** and sulfoxides. The IR results also rule out alternative intermediates, such as dimer structures (which may show more complicated isotopic shifts) and a sulfide cation radical–superoxide anion radical pair. We therefore conclude that the labile intermediate formed in sulfide photooxidation is a persulfoxide and that structure **1** best represents this molecule.[30]

Since diphenyl sulfide is known to be inert to oxidation by singlet oxygen,[2,3b] it is unlikely that these reactions involve it. A probable pathway to persulfoxide **1** is direct reaction from the excited donor–acceptor complex of the sulfide and oxygen, similar to the case of photooxidation of tetramethylethylene in a cryogenic oxygen matrix[16] and sulfides in solution.[7]

After this paper was submitted, Foote et al.[31] reported a theoretical study of products of reaction of singlet oxygen with H_2S and Me_2S. The infrared frequencies and intensities of a persulfoxide intermediate and the effect on the frequencies of substituting either one or both of the oxygens in a persulfoxide with ^{18}O were calculated. The calculated values agree with experimental data reported here.

Acknowledgment. We are indebted to Professor C. S. Foote for his valuable comments and discussion.

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(18) For IR measurement, sulfide and oxygen gas were deposited on a CsI plate at 13 K. IR absorption spectra were recorded on as Shimazu FT-IR 4000 spectrophotometer with 2 cm^{-1} resolution and 50 accumulations. The spectral range measured was 400–4000 cm.$^{-1}$ UV irradiation was carried out by means of a 500-W high pressure mercury lamp (USHIO). A water cell (20 cm) with quartz windows and a sharp-cut optical filter (Toshiba UV-D35 filter) were used at all times to remove the infrared radiation and to select exciting wavelengths (300–400 nm).

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(20) At temperatures higher than 40 K, the intense bands at ca. 1000 cm^{-1} disappeared and the oxygen matrix became very cloudy. Product analysis at room temperature shows the formation of diphenyl and methyl phenyl sulfoxide by means of mass and nmr spectral analysis.

(21) The stretching vibrations of the S–O bond can be calculated simply by the following equation,[22] by using the values 1.538 Å[3h] for the S–O bond length in unsubstituted thiirane persulfoxide: $\nu = {}^1/_2\,\pi c(f/(M_s{\cdot}M_o/M_n + M_s))^{1/2}, f = 1.86 \times 10^5/(r - 0.88)^3$, where ν = the stretching frequency (cm^{-1}); c = the velocity of light (cm/s); f = the force constant of bond (dyn/cm); r = the bond length (Å); M_s and M_o = the mass of sulfur atom and oxygen atom, respectively (g).

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(23) $^{18}O_2$ labeled oxygen was obtained from Amersham International.

(24) ^{18}O Labeled methyl phenyl sulfoxide (^{18}O content 30 atom %) was prepared by a literature method.[25] The IR absorption bands at 1050 and 1022 cm^{-1} are assigned to the stretching vibrations due to S–^{16}O and S–^{18}O group, respectively.

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(28) For a discussion of isotopic labeling experiments in the related structural problem of carbonyl oxide and dioxirane intermediate, see: (a) Bell, G. A.; Dunkin, I. R. *J. Chem. Soc., Chem. Commun.* **1983**, 1213. Dunkin, I. R.; Shileds, C. J. *J. Chem. Soc., Chem. Commun.* **1986**, 154. (b) Ganzer, G. A.; Sheridan, R. S.; Liu, M. T. H. *J. Am. Chem. Soc.* **1986**, *108*, 1517.

(29) It has been known that the isotope effect for an α substituent is generally small compared to the bond frequency: Halford, J. O. *J. Chem. Phys.* **1956**, *24*, 830.

(30) A proposed rearrangement of a persulfoxide intermediate **1** to a dioxathiirane intermediate[3g] **3** was not observed under the reaction condition.

(31) Jensen, F.; Foote, C. S., submitted for publication. We thank Prof. Foote for a prepublication copy of their manuscript.

Proton Transfer from Metal Hydrides to Metal Alkynyl Complexes. Remarkable Carbon Basicity of $(C_5H_5)(PMe_3)_2Ru—C{\equiv}C—CMe_3$

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The reactions of transition-metal hydrides with metal alkynyl compounds are virtually unexplored. The only previous systematic study is Lukehart's[1] synthesis of bridging vinylidene complexes from formal addition of a Pt–H bond across the carbon–carbon triple bond of several metal alkynyl compounds. Davison and Selegue[2] have shown that unsaturated carbon ligands bonded to late transition metals generally undergo β-attack by electrophiles and α-attack by nucleophiles. This suggested that metal vinylidene complexes might be formed by proton transfer from metal hydrides to metal alkynyl complexes. This communication reports the first kinetic and thermodynamic measurements on this type of reaction and provides evidence that certain ruthenium alkynyl complexes are remarkably strong carbon-centered bases.

The ruthenium methylvinylidene/metal anion complexes[3] ($\mathbf{1}^+$) precipitate from solution as yellow powders when toluene solutions of $(C_5H_5)(PMe_3)_2Ru—C{\equiv}C—CH_3$[4] and $(C_5H_5)M(CO)_3H$ (M = Cr, Mo, W) are combined. Thermolysis of the PF_6^- salt of $\mathbf{1}^+$ in acetonitrile at 95 °C results in release of the methylvinylidene ligand as propyne, with clean formation of the acetonitrile complex[3,5] $(C_5H_5)(PMe_3)_2Ru(CH_3CN)^+PF_6^-$ ($\mathbf{2}^+$). In contrast, thermolysis of metal anion salts of $\mathbf{1}^+$ produces cyclobutenylidene complex $\mathbf{3}^+$ in addition to $\mathbf{2}^+$. The formation of $\mathbf{3}^+$ can be accounted for by partial deprotonation of $\mathbf{1}^+$ by the metal anion base, thus regenerating the ruthenium alkynyl complex from which it was formed. The alkynyl complex and the methylvinylidene complex then combine to form $\mathbf{3}^+$ (as the $(C_5H_5)M(CO)_3^-$ salt). Independent synthesis[3] and isolation (73% yield) of the intensely colored orange complex $\mathbf{3}^+PF_6^-$ ($\epsilon = 1.9 \times 10^4$ M^{-1} cm^{-1} at λ_{max} = 428 nm) was accomplished by reaction of $\mathbf{1}^+PF_6^-$ with

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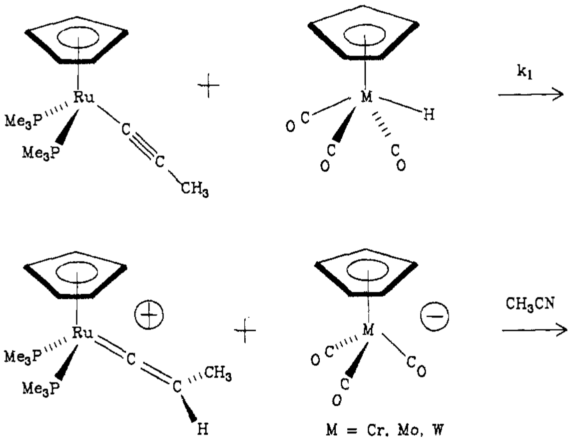

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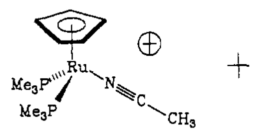

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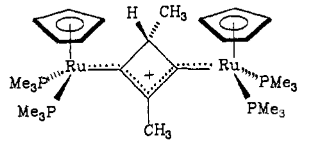


3

$(C_5H_5)(PMe_3)_2Ru—C≡C—CH_3$. Similar iron complexes have been prepared previously by related routes.[6]

The proton-transfer reaction leading to $\mathbf{1}^+Mo^-$ and $\mathbf{1}^+W^-$ was studied by stopped-flow kinetics in acetone and acetonitrile and was found to conform to the second-order rate law $d[\mathbf{1}^+]/dt = k[Ru—C≡C—CH_3][MH]$. The reaction rate of the molybdenum hydride ($pK_a = 13.9$)[7] is about 10 times faster than that of the less acidic tungsten hydride ($pK_a = 16.1$);[7] see Table I.

The pK_a of $(C_5H_5)(PMe_3)_2Ru{=}C{=}C(H)CMe_3^+$ in CH_3CN was determined to be 20.8 (±0.2) by titration of $(C_5H_5)(PMe_3)_2Ru—C≡C—CMe_3$ with PhOH ($pK_a = 26.6$).[8] This indicates that the ruthenium alkynyl complex is a remarkably strong carbon-centered base, being significantly stronger than either 1,8-bis(dimethylamino)naphthalene[9] ("proton sponge") or NEt_3 (pK_a of $HNEt_3^+ = 18.5$ in CH_3CN).[7b,10] Proton transfers to carbon have been well-studied in organic chemistry in the context of acid-catalyzed hydration of alkenes[11,12] and ketenes,[13] ketonization of enols,[14] hydrolysis of vinyl ethers,[11,15] etc., but proton transfers to carbon in organometallic complexes have received little attention.[16] The availability of kinetic and thermodynamic information for protonation of the ruthenium alkynyl complexes allows comparison to the kinetic measurements of Norton et al.[16] on the rate of proton transfer from $(C_5H_5)(CO)_3WH$ to amine bases. The proton transfer rate from this tungsten hydride to $(C_5H_5)(PMe_3)_2Ru—C≡C—CH_3$ is only 10 times faster than the rate of proton transfer of the same hydride to aniline, despite the fact that the free-energy change for the former reaction is favorable (by about 6.4 kcal/mol) while the latter is unfavorable (by 7.5 kcal/mol). This small difference in rate (compared to a difference in thermodynamic driving force of about 14 kcal/mol) reflects a large intrinsic barrier[17] to proton transfer to the metal alkynyl complex. This is due to the substantial structural and electronic reorganization[17a,b] which accompanies the conversion of the neutral ruthenium alkynyl compound into the cationic vinylidene complex.

Table I. Second-Order Rate Constants (k_1 in Eq 1) for Proton Transfer from $HM(CO)_3(C_5H_5)$ to $(C_5H_5)(PMe_3)_2Ru—C≡C—CH_3$, Determined by Stopped-Flow Kinetics at 25 °C

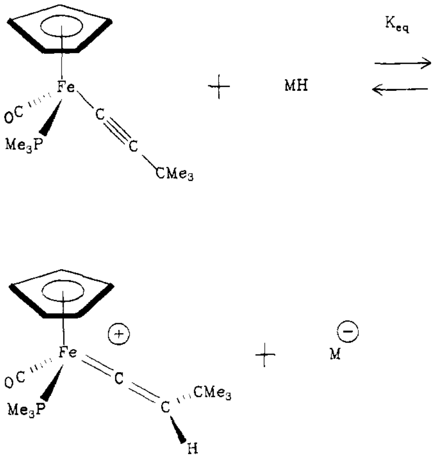
$HM(CO)_3(C_5H_5)$	solvent	k_1, $M^{-1}\ s^{-1}$
W	acetonitrile	2.5×10^3
W	acetone	1.5×10^3
Mo	acetone	1.4×10^4

Table II. Thermodynamic Data for the Proton-Transfer Reaction from Metal Hydrides to $(C_5H_5)(CO)(PMe_3)Fe—C≡C—CMe_3$ (Eq 2)

	in CD_3CN with no added electrolyte[a]		ionic strength = 0.5 M (0.5 M NBu_4BF_4 added to CD_3CN)	
	$\Delta H°$, kcal/mol	$\Delta S°$, eu	$\Delta H°$, kcal/mol	$\Delta S°$, eu
$HCr(CO)_3(C_5H_5)$	-8.0 (2)	-25.7 (8)	-7.4 (3)	-22 (1)
$HMo(CO)_3(C_5H_5)$	-5.3 (2)	-20.5 (7)	-4.4 (2)	-14.5 (7)
$DMo(CO)_3(C_5H_5)$	-5.6 (2)	-19.7 (7)		
$HMn(CO)_5$	-2.8 (1)	-15.3 (3)	-2.5 (1)	-11.0 (4)

[a] Actual ionic strength = $[(C_5H_5)(CO)(PMe_3)Fe{=}C{=}C(H)CMe_3]^+$, I = 0.03 - 0.08 M for these experiments.

Proton transfer from metal hydrides to the iron alkynyl complex[3] $(C_5H_5)(CO)(PMe_3)Fe—C≡C—CMe_3$ generates two isomers of the cationic iron vinylidene complex[3] (only one isomer is shown) which exist in a temperature-independent 84:16 mixture. Compared to the bis(trimethylphosphine)ruthenium compounds discussed above, the equilibrium constant for this proton transfer reaction is much smaller[18] and can be directly measured by NMR. The ΔH^0 and ΔS^0 were determined by evaluation of the temperature dependence of the equilibrium constant (see Table II).



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[18] The pK_a of $(C_5H_5)(CO)(PMe_3)Fe{=}C{=}C(H)CMe_3^+$ in CH_3CN was found to be 13.6 (±0.3).

Measurements were carried out both at a constant ionic strength of 0.5 M and also in the absence of any added electrolyte. The equilibrium constant increases with decreasing temperature. Lower ΔH^0 values are observed for the more acidic hydrides, while the negative values of ΔS^0 are expected due to greater solvation of the ionic products. Thermolysis of the iron vinylidene cation (BF_4^- counterion) in CH_3CN at 57 °C releases *tert*-butylacetylene and leads to the formation of $(C_5H_5)(CO)(PMe_3)Fe(CH_3CN)^+BF_4^-$, which was isolated as red needles in 78% yield.[3]

Acknowledgment. This research was carried out at Brookhaven National Laboratory under contract DE-AC02-76CH00016 with the U.S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences. I thank Drs. Carol Creutz, Mark Andrews, Ed Samsel, and Jack Norton for helpful discussions and Dr. Bruce Brunschwig for assistance with the stopped-flow kinetics.

Supplementary Material Available: Spectroscopic and analytical data for 1^+ (PF_6^-, Cr^-, Mo^-, W^- salts), $2^+PF_6^-$, $3^+PF_6^-$, $(C_5H_5)(CO)(PMe_3)Fe{-}C{\equiv}C{-}CMe_3$, $(C_5H_5)(CO)(PMe_3)Fe{=}C{=}C(H)CMe_3{}^+BF_4^-$, and $(C_5H_5)(CO)(PMe_3)Fe(CH_3CN)^+BF_4^-$ (3 pages). Ordering information is given on any current masthead page.

Para Hydrogen Induced Polarization in Hydrogenation Reactions

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Since 1969, the occurrence of enhanced NMR absorptions and emissions known as CIDNP has been viewed as definitive evidence of a radical pair mechanism.[1-3] Recently, we reported that the binuclear complex $Rh_2H_2(CO)_2(dppm)_2$ hydrogenates alkynes with CIDNP observed in the product olefin resonances.[4] Through the use of ^{13}C and ^2H labeled substrates, we showed that the polarization process did *not* involve the intermediacy of organic radicals, thus differing from other observations of CIDNP in hydrogenations involving mononuclear organometallic hydrides.[5-8] We now report results with other complexes and substrates including simple olefins and show that the polarizations we observe, and those described earlier,[4] arise from para H_2. The notion that hydrogenation reactions using para H_2 can generate polarized products has recently been proposed and demonstrated by Weitekamp.[9] This means of developing polarization, which does not require radicals of any type, promises to be a highly useful tool for the study of hydrogenation reactions and H_2 oxidative additions.

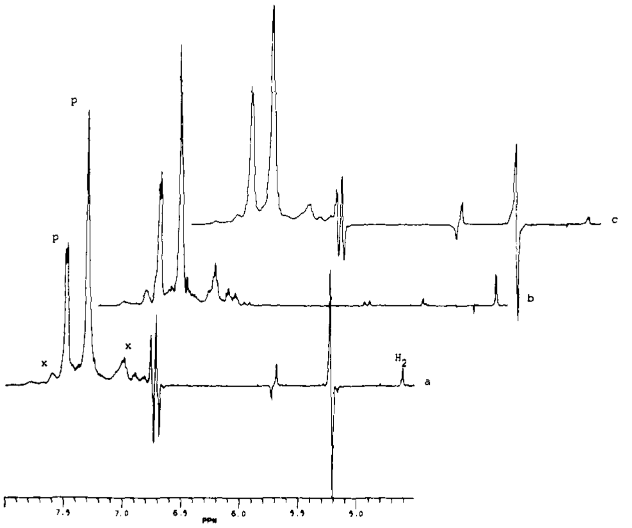
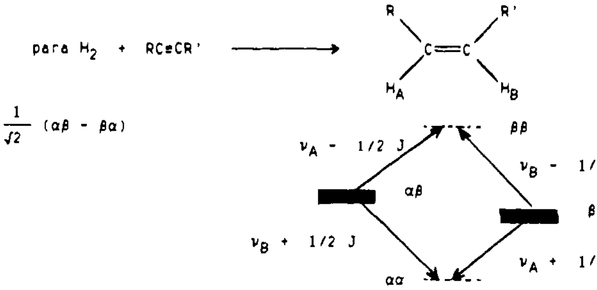


Figure 1. ^1H NMR spectra at 400 MHz showing para H_2 induced polarization in the resonances of styrene from the reaction of $[Rh_3Cl_2H_2(CO)_2((Ph_2PCH_2)_2PPh)_2]^+$ with $PhC{\equiv}CH$ in $CDCl_3$ under H_2: (a) after storage at −196 °C under H_2; (b) after storage at −196 °C under vacuum followed by addition of tank H_2; (c) after storage at −196 °C under vacuum followed by addition of para enriched H_2. The resonances marked "x" are due to the catalyst complex and those marked "p" are due to excess $PhC{\equiv}CH$.

According to the Weitekamp proposal,[9] para H_2 induced polarization can arise when H_2 is transferred pairwise to a substrate to yield a product in which the two transferred protons are magnetically distinct. If the reaction occurs fast relative to proton relaxation, then the transferred protons will initially reflect the nuclear spin populations of the starting dihydrogen. This is shown schematically in eq 1 for hydrogenation of an internal alkyne with



(1)

para H_2. Since only the $\alpha\beta$ and $\beta\alpha$ states of the product olefin correlate with the para H_2 nuclear spin function, these states will be overpopulated relative to a normal Boltzmann distribution (as shown in the diagram of eq 1), giving rise to polarized A/E or

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