Table I. Oxygen Affinity and k_{off} Rate Data for Sperm Whale Mb

Mb sample[a]	$P_{1/2}(O_2)$ at 25 °C,[b] mmHg	n[c]	k_{off} at 25 °C,[b] s^{-1}
native	0.71 ∓ 0.01 (4)	0.99	22.7 ∓ 0.7 (3)
native[d]	0.72 ∓ 0.04 (2)	1.00	
reequilibrated[e]	0.69 ∓ 0.02 (2)	1.00	23.4 ∓ 0.9 (3)
55:45 mixture	0.29 ∓ 0.03 (4)	0.85	24.7 ∓ 1.4 (3)
65:35 mixture	0.37 ∓ 0.03 (2)	0.90	
75:25 mixture	0.47 ∓ 0.02 (3)	0.92	

[a] Ratio of heme orientations as depicted in A and B of Figure 1; native and reequilibrated Mb has ~10:1 ratio.
[b] Number of determinations are given in parentheses.
[c] Hill coefficient as determined from slope in C of Figure 1.
[d] Sample was held at pH 5.1 for 2 h to simulate conditions for the disordered reconstituted samples.
[e] Sample was reequilibrated to the native (~10:1) ratio from a 55:45 disordered mixture.

earlier.[5]

The measured[10] O_2 affinities are illustrated in the usual Hill plots in C of Figure 1. For the 55:45 ratio, the slope (Hill coefficient, *n*) is less than unity (0.85), as expected for protein components with different O_2 affinities. The slopes increase as the heme disorder equilibrates and reach unity for the native and reequilibrated reconstituted protein. The data points for the latter two samples are essentially indistinguishable, and the $P_{1/2}$s agree with published values.[13] The O_2 affinities, as reflected in the half-saturation pressure, $P_{1/2}(O_2)$, for each sample, are listed in Table I. The increase in $P_{1/2}(O_2)$ upon equilibration dictates that the "wrong" heme orientation has a significantly higher affinity. Regression analysis to the Hill equation of the $P_{1/2}$s as a function of the composition yields $P_{1/2}$(major) = 0.83 and $P_{1/2}$(minor) = 0.07 mmHg. Thus the apparent $P_{1/2}$ measured for an equilibrium mixture will overestimate the affinity of the X-ray characterized heme orientation by ca. 15%.

Alterations in $P_{1/2}$ must result from a different k_{off} or k_{on} for O_2 binding, or both. The measured k_{off}s for the native and 65:35 mixtures were identical, indicating that at least one component of the latter has normal O_2 dissociation characteristics. Long-term detector instability of our stopped-flow spectrophotometer prevented us from detecting slow off rates ($t_{1/2} > 250$ ms).

The present characterization of a significant effect of heme orientation on O_2 affinity in Mb coupled with our earlier demonstration of such disorder in several native hemoproteins[5,14,15] suggest a careful reinvestigation of the physicochemical properties for hemoproteins reconstituted with modified hemin[12,16,17] for signs of variable heme disorder. The substantial effect of heme disorder on O_2 affinity has importance not only in illustrating the correct function for a unique protein prosthetic group conformation but may have implications for the physiological role of Mb. The rate of the interconversion of the two species formed in the heme-apoMb reaction, contrary to earlier reports,[18] is extremely slow at physiological pH.[7,8] In the absence of an enzyme-mediated reconstitution dictating a unique heme orientation, heme disorder may be expected to influence the in situ Mb O_2 affinity. Calculations of the contribution of Mb to the in vivo facilitated O_2 flux[3] must consider the ratios of the two Mb conformations and the resulting effective $P_{1/2}$.

Acknowledgment. This work was supported by grants from the National Science Foundation, CHE-81-08766, the National Institutes of Health, HL-16087, and the Calfironia Sea Grant Program.

Registry No. Heme, 14875-96-8; oxygen, 7782-44-7.

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(13) Reference 4, chapter 10.

(14) La Mar, G. N.; Smith, K. M.; Gersonde, K.; Sick, H. *J. Biol. Chem.* **1980**, *255*, 66.

(15) La Mar, G. N.; Burns, P. D.; Jackson, J. T.; Smith, K. M.; Langry, K. C.; Strittmatter, P. *J. Biol. Chem.* **1981**, *236*, 6075.

(16) Asakura, T.; Lau, P. W.; Sono, M.; Adachi, K.; Smith, J. J.; McCray, J. A. In "Hemoglobin and Oxygen Binding"; Ho, C., Ed.; Elsevier Biomedical: New York, 1982; p 177.

(17) Kawabe, K.; Imaizumi, K.; Yoshida, Z.; Imai, K.; Tyuma, I. *J. Biochem.* **1982**, *92*, 1713.

(18) Gibson, Q. H.; Antonini, E. *J. Biol. Chem.* **1963**, *238*, 1384.

Migratory Insertion within a Cationic Alkylidene-Aryl Complex of Tungsten

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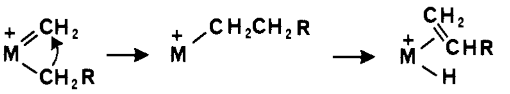
We have recently shown that alkylidene ligands in cationic tungsten complexes insert into cis tungsten–alkyl linkages, and we have described the reaction as a migration of the alkyl group, with its bonding electron pair, on to an unsaturated carbon which has been rendered electrophilic by the positive charge (eq 1, M



(1)

= W(η-C_5H_5)$_2$, R = H or CH_3).[1,2] The facility of such reactions is supported by reports of insertion within other cationic alkylidene–alkyl complexes, including both iridium[3] and, more recently, ruthenium[4] phosphine complexes, and by earlier reports of facile migratory insertion in niobium carbene complexes rendered electrophilic by the electron-withdrawing nature of the zirconoxy substituents.[5]

The transitory alkylidene–alkyl complexes were generated by hydrogen atom abstraction from paramagnetic species of the type $[W(\eta\text{-}C_5H_5)_2(CH_3)R]^{+\cdot}$, and, since such substrates are potentially available with a wide range of substituents R, we have recently been exploring the generality of the insertion reaction by examining the reactions of other paramagnetic tungstenocene alkyls with the trityl radical.[6] We now wish to report that this approach has led to the first example of insertion of an alkylidene or carbene ligand into a transition-metal–aryl bond.

A 17-electron precursor for a cationic alkylidene–aryl complex was prepared from $[W(\eta\text{-}C_5H_5)_2(CH_3)I]$[7] as shown in eq 2.

$$[W(\eta\text{-}C_5H_5)_2(CH_3)I] \xrightarrow{PhMgBr} [W(\eta\text{-}C_5H_5)_2(CH_3)Ph] \xrightarrow{[Fe(\eta\text{-}C_5H_5)_2]PF_6} [W(\eta\text{-}C_5H_5)_2(CH_3)Ph]PF_6 \quad (2)$$

Treatment of a solution of the iodide (2.14 g, 4.70 mmol) in 25 mL of diethyl ether with 4.9 equiv of 1.15 M PhMgBr in diethyl ether resulted in slow (19 h) discharge of the intense green color and formation of a red solution. Hydrolysis followed by extraction with toluene gave a red-orange material which was partially purified by chromatography on deactivated Al_2O_3 using pentane eluant. Removal of the solvent and of the volatile biphenyl contaminant under vacuum gave spectroscopically pure $[W(\eta\text{-}C_5H_5)_2(CH_3)Ph]$[8] as an orange powder (74%) which could be recrystallized from pentane at −60 °C as orange-red plates.

The neutral methyl–phenyl complex is thermally stable but can be readily oxidized to the corresponding radical cation. This was accomplished synthetically by using 1 equiv of ferrocinium hexafluorophosphate added at −78 °C as a 0.014 M solution in CH_2Cl_2 to a −78 °C solution of $[W(\eta\text{-}C_5H_5)_2(CH_3)Ph]$ (0.20 g, 0.50 mmol) in CH_2Cl_2 (10 mL). After 2 h at −78 °C the stirred mixture was warmed to −45 °C and the solvent removed. Fer-

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[†] Fellow of the Alfred P. Sloan Foundation, 1982–1984.

(1) Hayes, J. C.; Pearson, G. D. N.; Cooper, N. J. *J. Am. Chem. Soc.* **1981**, *103*, 4648.

(2) Hayes, J. C.; Cooper, N. J. *J. Am. Chem. Soc.* **1982**, *104*, 5570.

(3) Thorn, D. L.; Tulip, T. H. *J. Am. Chem. Soc.* **1981**, *103*, 5984.

(4) Kleitzein, H.; Werner, H.; Serhadli, P.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 46.

(5) Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1981**, *103*, 2650.

(6) (a) Copenhauer, J. W.; Roy, M. F.; Marvel, C. S. *J. Am. Chem. Soc.* **1935**, *57*, 1311. (b) McBride, J. M. *Tetrahedron* **1974**, *30*, 2009 and references therein.

(7) Cooper, N. J.; Green, M. L. H.; Mahtab, R. *J. Chem. Soc., Dalton Trans.* **1979**, 1557.

(8) ^1H NMR (acetone-d_6, 80 MHz): δ 7.65–7.50, 6.85–6.70 (c, 5 H, C_6H_5), 4.63 (s, 10 H, 2 C_5H_5), 0.07 (s, satellites $J_{^{183}W}$ = 5.6 Hz, 3 H, CH_3). Mass spectrum (parent ion, ^{184}W), *m/e* 406. Anal. Calcd for $C_{17}H_{18}W$: C, 50.26; H, 4.48. Found (Galbraith Laboratories, TN): C, 50.29; H, 4.17.

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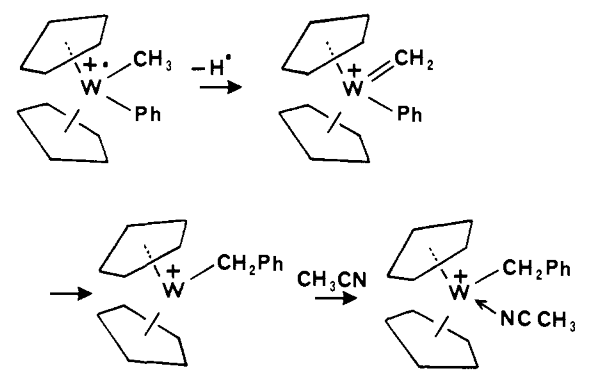
Scheme I



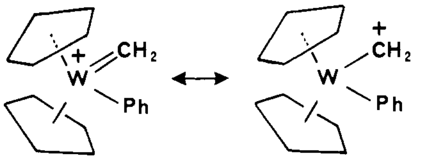
rocene was removed by trituration with toluene and the brick-red powder obtained was dried under vacuum to give $[W(\eta\text{-}C_5H_5)_2(CH_3)Ph]PF_6$ (0.23 g, 0.40 mmol ≡ 86%). Analytical samples were obtained in 50% yield by rapidly concentrating a CH_2Cl_2 solution and collecting the resulting red needles by decantation, but the crude salt, identical by IR and ESR with recrystallized material, was typically used for subsequent experiments without further purification. ^1H NMR spectra showed the absence of diamagnetic tungstenocene derivatives, and the compound was characterized by analysis and by ESR.[9] This showed the presence of a single major paramagnetic species with an $\langle g \rangle$ value similar to that observed for other tungstenocene dialkyl cations[2,7] and somewhat higher than the values reported for tungstenocene dihalo cations.[10] Chemical characterization of the complex included reduction back to $[W(\eta\text{-}C_5H_5)_2(CH_3)Ph]$ (ca. 60%) using saturated aqueous KOH/acetone.[11]

Hydrogen atom abstraction from $[W(\eta\text{-}C_5H_5)_2(CH_3)Ph]PF_6$ was accomplished by stirring the salt (0.12 g, 0.22 mmol) in CH_3CN (60 mL) with an excess (0.57 mmol) of the trityl radical dimer[6] at room temperature. After 2.5 h the intense red color of the cation was replaced by an orange color. The solvent was removed and the triphenylmethane formed (^1H NMR) washed off together with excess dimer (diethyl ether). The organometallic product was recrystallized from CH_2Cl_2 as brown-orange rods and plates by slow concentration of a saturated solution. Analysis and ^1H NMR showed that the product was the acetonitrile complex $[W(\eta\text{-}C_5H_5)_2(CH_2Ph)(NCCH_3)]PF_6$[12] (56%).

Formation of $[W(\eta\text{-}C_5H_5)_2(CH_2Ph)(NCCH_3)]PF_6$ (Scheme I) presumably follows generation of a methylidene–aryl cation which undergoes migratory insertion to give a 16-electron benzyl complex. Since this species lacks a β-hydrogen (unlike its ethyl or propyl analogues[1,2]), it cannot form an alkene hydride complex (eq 1), but instead coordinates a solvent molecule to give the observed product. The acetonitrile complex can also be prepared from a preformed benzyl complex by heating a solution of $[W(\eta\text{-}C_5H_5)_2(C_2H_4)CH_2Ph]PF_6$[13] in acetonitrile at 45 °C. Solvent displacement of ethylene is complete within 48 h, and the product can be isolated in 44% recrystallized yield.

It is possible that the polar solvent participates more directly in the insertion step than is indicated in Scheme I. Coordination of CH_3CN to the cationic tungsten center could be responsible, for example, for the difference between the reactivity observed for $[W(\eta\text{-}C_5H_5)_2(CH_2)Ph]^+$ and that reported for $[Nb(\eta\text{-}C_5H_5)_2CH\{OZrH(\eta\text{-}C_5Me_5)_2\}Ph]$;[5] although this complex contains an electrophilic carbene ligand, it does not undergo migratory insertion (for either kinetic or thermodynamic reasons) under the conditions examined.

Simple bonding considerations (eq 3) suggest that a useful analogy can be drawn between migratory insertions in cationic alkylidene–alkyl complexes and 1,2-alkyl shifts within carbonium ions.[14] When such Wagner–Meerwein rearrangements involve



(3)

aryl migration it is usually assumed that their facility reflects the ability of the aromatic p-orbital on the migrating carbon to interact simultaneously with the carbon atoms at both termini of the migration, and it is to be expected that this bridging ability would also facilitate aryl migration in cationic alkylidene–aryl complexes of transition metals. This pathway does, however, require that the aryl group be oriented with the ring perpendicular to the plane containing the $M{=}CH_2$ bond and the migrating carbon, and this arrangement could result in unfavorable steric interactions with other ligands. In the tungstenocene system such contacts do not apparently prevent the migration, although the steric interactions observed between the ring hydrogens and the ethylidene ligand in $[Ta(\eta\text{-}C_5H_5)_2(CHCH_3)CH_3]$[15] would suggest that similar interactions with the perpendicular phenyl in $[W(\eta\text{-}C_5H_5)_2(CH_2)Ph]^+$ are probably marked.

Acknowledgment. We thank the National Science Foundation (Grant CHE830238) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their financial support.

Registry No. $W(\eta\text{-}C_5H_5)_2(CH_3)I$, 71531-99-2; $W(\eta\text{-}C_5H_5)_2(CH_3)Ph$, 89710-99-6; $[W(\eta\text{-}C_5H_5)_2(CH_3)Ph]PF_6$, 89711-01-3; $[W(\eta\text{-}C_5H_5)_2(CH_2Ph)(NCCH_3)]PF_6$, 89711-03-5; $[W(\eta\text{-}C_5H_5)_2(CrH_4)CH_2Ph]PF_6$, 53770-69-7.

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[9] ESR (CH_2Cl_2, 25 °C,, 9.439 GHz): $\langle g \rangle = 2.049$. IR (KBr): 3133 s, 3068 w, 3052 mw, 2970 w br, 2902 w, 1571 m, 1560 w, 1438 s br, 1420 ms, 1385 m, 1337 w, 1316 w, 1304 w, 1245 w, 1211 w, 1128 w, 1070 mw, 1025 m sh, 1019 ms, 1000 m, 969 mw, br, 850 vs br, 741 s, 703 ms, 552 s, 490 w, 365 mw br. Anal. Calcd for $C_{17}H_{18}F_6PW$: C, 37.04; H, 3.30. Found (Galbraith Laboratories, TN): C, 37.07; H, 3.34.

[10] Lindsell, W. E. *J. Chem. Soc., Dalton Trans.* **1975**, 2548.

[11] The tungstenocene dialkyl radical cations which we have prepared previously[2,7] are characteristically reduced to the parent W(IV) complexes under these conditions.

[12] ^1H NMR (acetone-d_6, 80 MHz): δ 7.20–7.00 (c, 5 H, C_6H_5), 5.43 (s, 10 H, $2C_5H_5$), 2.81 (s, 3 H, CH_3CN), 2.65 (s, satellites $J_{^{183}W} = 8.1$ Hz, 2 H, CH_2). Anal. Calcd for $C_{19}H_{20}F_6NPW$: C, 38.60; H, 3.42. Found (Schwarzkopf Laboratories, NY): C, 38.33; H, 3.52.

[13] Benfield, F. W. S.; Cooper, N. J.; Green, M. L. H. *J. Organomet. Chem.* **1974**, *76*, 49.

[14] Kirmse, W. *Top. Curr. Chem.* **1979**, *80*, 125.

[15] Sharp, P. R.; Schrock, R. R. *J. Organomet. Chem.* **1979**, *171*, 43.

Spectroscopy and Photochemistry of Binuclear Iridium(I) Complexes

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Received December 23, 1983

Extensive spectroscopic studies on $Rh_2b_4^{2+}$ (b is 1,3-diisocyanopropane) and $Pt_2(P_2O_5)_4H_8^{4-}$ indicate that the $^1A_{1g}$ (D_{4h}) ground state is weakly metal–metal bonding, and the lowest electronic excited states are a triplet ($^3A_{2u}$) and a singlet ($^1A_{2u}$) derived from the $(d\sigma)^2(d\sigma^*)^1(p\sigma)^1$ electronic configuration.[2] Interestingly, the luminescent $^3A_{2u}$ excited state, which is strongly metal–metal bonding,[2c,3] undergoes reversible electron-transfer

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[2] (a) Rice, S. F.; Milder, S. J.; Gray, H. B.; Goldbeck, R. A.; Kliger, D. S. *Coord. Chem. Rev.* **1982**, *43*, 349 and references therein. (b) Che, C-M.; Butler, L. G.; Gray, H. B. *J. Am. Chem. Soc.* **1981**, *103*, 7796. (c) Rice, S. F.; Gray, H. B. *Ibid.* **1983**, *105*, 4571.

[3] (a) Rice, S. F.; Gray, H. B. *J. Am. Chem. Soc.* **1981**, *103*, 1593. (b) Dallinger, R. F.; Miskowski, V. M.; Gray, H. B.; Woodruff, W. H. *Ibid.* **1981**, *103*, 1595. (c) Che, C-M.; Butler, L. G.; Gray, H. B.; Crooks, R. M.; Woodruff, W. H. *Ibid.* **1983**, *105*, 5492.

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