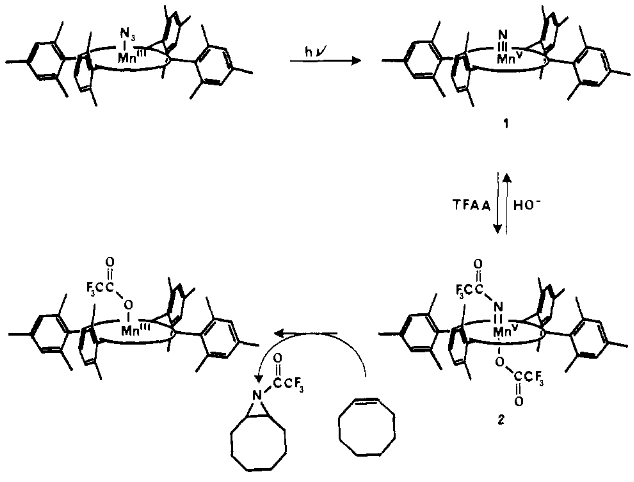
Scheme I



to undergo nitrogen-transfer reactions with organic compounds.[11] We report here the first example of metal nitride activation to give aziridines in the presence of double bonds; the aza analogue of epoxidation.

Irradiation of azido(5,10,15,20-tetramesitylporphyrinato)-manganese(III) in benzene[8] for 4 h followed by column chromatography on basic alumina afforded red-purple crystals of nitrido(5,10,15,20-tetramesitylporphyrinato)manganese(V) (**1**),[12] TMPMn(V)N) in 80% yield. This manganese(V) nitride was found to be diamagnetic, consistent with a low-spin d^2 electronic configuration. Accordingly, the ^{1}H NMR spectrum of **1** showed sharp resonances in the normal range of chemical shifts (Figure 1). The visible spectrum of **1** showed a strong and sharp Soret maximum at 420 nm (Figure 2a). TMPMn(V)N (**1**) is an extraordinarily stable complex and was unaffected by iodide ion, olefins, or triphenylphosphine. Compound **1** was also found to be resistant to acid, base, and oxygen.

TMPMn(V)N did react in methylene chloride with trifluoroacetic anhydride at room temperature to give a new, green, paramagnetic complex **2**. Thus, reaction of **1** with a 20-fold excess of trifluoroacetic anhydride for 40 min afforded a soln. that showed ^{1}H NMR resonances at δ −23.02 (β-pyrrole H), 5.67 (*p*-Me), 10.84 (*o*-Me), and 26.13 (*m*-H). Weaker resonances due to TMPMn(III) trifluoroacetate could also be discerned. The visible spectrum of the intermediate **2** showed a Soret band at 409 nm (Figure 2b).

Several lines of evidence support an acylimidomanganese(V) trifluoroacetate[13] for **2**: (i) The IR spectrum of solutions of **2** showed new bands at 1697 and 1745 cm^{-1} for the trifluoroacetate and imidotrifluoroacetate groups, respectively. The lack of any band near 1270 cm^{-1} argues against a porphyrin π-cation radical.[14] (ii) The ^{1}H NMR spectrum of a reaction mixture of **1** and 10 equiv of trifluoroacetic anhydride exhibited unusual dynamic behavior. The sharp proton resonances due to **1** were observed to broaden and shift *gradually* with time toward the resonance positions for **2** (Figure 1), while the visible spectrum showed only the appearance of **2** at the expense of **1**. Thus, the NMR spectra of **1** and **2** are averaged by a rapid self-exchange process. N-acylation of **1** and facile, reversible acyl transfer from **2** to **1** would explain this observation. (iii) The reaction of **2** with tetrabutylammonium hydroxide in methylene chloride regenerated the starting nitride (**1**). (iv) The N-trifluoroacetyl group in **2** would be expected to decrease the π-donor properties of the axial nitrogen ligand. The conversion from a diamagnetic configuration for **1** to a paramagnetic state for **2** is consistent with the resultant lowering of the d_{xz} and d_{yz} orbitals of manganese. Such a lowering is evident in the $(d_{xz},d_{yz})^4(d_{xy})^1$ configuration for the closely related TPPMn(III) nitrosyls.[15] (v) The addition of cyclooctene to solutions of **2** gave TMPMn(III)TFA and the (trifluoroacetyl)-aziridine of cyclooctene.[16]

In a typical reaction, 30 mg of TMPMn(V)N (**1**) was dissolved in dry, redistilled dichloromethane that contained an 11-fold excess of cyclooctene. The addition of 1.2 equiv of trifluoroacetic anhydride caused the reaction mixture to turn from red to green after 30 min at room temperature. Analysis of the reaction mixture by GLPC showed that 9-(trifluoroacetyl)-9-azabicyclo[6.1.0]-nonane was produced in 82–94% yield by comparison of the isolated product to an authentic sample.[17] Treatment of the reaction mixture with aqueous base and extraction with dilute HCl afforded the parent aziridine in similar yield.

A mechanism consistent with the nitrogen activation and transfer described here is presented in Scheme I.[18]

Acknowledgment. Financial support of this research by the National Science Foundation (CHE-81-06064) is gratefully acknowledged. The National Science Foundation provided funds for the purchase of a 360-MHz NMR spectrometer.

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[10] Mansuy, D.; Battioni, P.; Mahy, J. P. *J. Am. Chem. Soc.* **1982**, *104*, 4487–4489.

[11] For an example of alkane amidation see: Breslow, R.; Gellman, S. H. *J. Chem. Soc., Chem. Commun.* **1982**, 1400–1401.

[12] (a) Anal. Calcd for $C_{56}H_{52}N_5Mn$ (850.01); **1**: C, 79.13; H, 6.17; N, 8.24; Mn, 6.46. Found: C, 78.98; H, 6.30; N, 8.26; Mn, 6.36. MS (EI, 70 eV), *m/e* (relative intensity) 851 (0.18), 850 (0.60), 849 (1.0) (M$^+$); IR $\nu_{\mathrm{Mn{\equiv}N}}$ 1048 cm^{-1}. (b) Preliminary X-ray data for **1** confirm the assigned structure: Yamauchi, M.; Butler, W.; unpublished results.

[13] An acylnitrenomanganese(III) structure or a nitrogen-bridged species would be functionally equivalent to **2**; Callot, H. J.; Chevier, B.; Weiss, R. *J. Am. Chem. Soc.* **1978**, *100*, 4733–4741.

[14] Shimomura, E. T.; Phillippi, M. A.; Goff, H. M.; Scholz, W. F.; Reed, C. A. *J. Am. Chem. Soc.* **1981**, *103*, 6778.

[15] Wayland, B. B.; Olson, L. W.; Siddiqui, Z. U. *J. Am. Chem. Soc.* **1976**, *98*, 94–98.

[16] for reviews of nitrene reactions see: Lwowski, W., Ed. "Nitrenes," Wiley: New York, 1970.

[17] (a) Hassner, A.; Matthews, G. J.; Fowler, F. W.; *J. Am. Chem. Soc.* **1969**, *91*, 5046–5054. (b) Fowler, F. W.; Hassner, A.; Levy, L. A. *Ibid.* **1967**, *89*, 2077–2082.

[18] The synthetic scope of this reaction is under current investigation. Cyclooctene is at present the most favorable case.

Ring Methyl to Phosphorus Hydrogen Shifts in Pentamethylcyclopentadienyl-Substituted Phosphorus Cations: Parallel between Main-Group and Transition-Metal Chemistry

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The activation of C–H bonds by d- and f-block elements is a topic of considerable current importance.[1] We now report (i) C–H bond activation by a main-group element and (ii) evidence for the first polyhedral phosphorus cations with only P–C bonds.[2]

The η^1 attachment of the Me_5C_5 ring in $(Me_5C_5)(t\text{-Bu})PCl$ (**1**)[3] is apparent from the $^{13}C\{^1H\}$ NMR (50.31 MHz) spectrum in the methyl and ring carbon regions: Me_a (d, δ 20.8, $J_{PCC} = 16.5$ Hz), Me_b or $Me_{b'}$ (s, δ 13.6 or s, δ 12.2), Me_c and $Me_{c'}$ (s, δ 11.3), C_a (d, δ 61.4, $J_{PC} = 49.4$ Hz), C_b or $C_{b'}$ (d, δ 136.7, $J_{PCC} = 39.0$ Hz or d, δ 136.8, $J_{PCC} = 19.2$ Hz), C_c and $C_{c'}$ (s, δ 135.5).

Treatment of **1** with a stoichiometric quantity of Al_2Cl_6 in CH_2Cl_2 solution at 0 °C results in Cl$^-$ abstraction as demonstrated by the detection of $AlCl_4^-$ as the sole aluminum-containing product in ^{27}Al NMR experiments.[4] Production of the cation,

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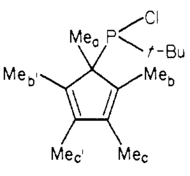
[1] See, for example: Parshall, G. W. *Acc. Chem. Res.* **1975**, *8*, 113. Parshall, G. W. *Catalysis* **1977**, *1*, 335. Webster, D. E. *Adv. Organomet. Chem.* **1977**, *15*, 147. Green, M. L. H. *Pure Appl. Chem.* **1978**, *50*, 27.

[2] The only previously synthesized polyhedral phosphorus cation featured conjugative stabilization via an amido group. Baxter, S. G.; Cowley, A. H.; Mehrotra, S. K. *J. Am. Chem. Soc.* **1981**, *103*, 5572.

[3] Jutzi, P.; Saleske, H.; Nadler, D. *J. Organomet. Chem.* **1976**, *118*, C8.



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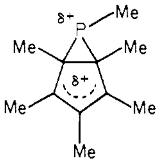
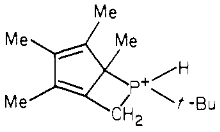
$[(Me_5C_5)(t\text{-}Bu)P]^+$ (**2**), is evident from the >70 ppm downfield ^{31}P chemical shift accompanying Cl^- removal: $^{31}P\{^1H\}$ NMR (36.43-MHz) **1** (s, δ +168), **2** (s, δ +240). The corresponding $(Me_3Si)_2CH$-substituted cation, $\{(Me_5C_5)[(Me_3Si)_2CH]P\}^+$ (**3**), was produced by aluminum chloride promoted Cl^- abstraction from $(Me_5C_5)[(Me_3Si)_2CH]PCl$ (**4**):[5] $^{31}P\{^1H\}$ NMR (36.43 MHz) **3** (s, +265.9), **4** (s, +171.0). Corroborative evidence for the **4** → **3** transformation is provided stereochemically. Compound **4** features a chiral center at phosphorus and hence exhibits diastereopy in the $(Me_3Si)_2CH$ group: ^1H NMR (90.0 MHz) Me_3Si (s, 9 H, δ 0.32), Me_3Si' (d, 9 H, δ 0.11, J_{PCSiCH} = 1.5 Hz). Cation **3** lacks such a chiral center; therefore, the Me_3Si groups are equivalent (s, 18 H, δ 0.24). The ring and Me carbons of cations **2** and **3** remain equivalent down to −90 °C in ^{13}C and ^1H NMR experiments: $^{13}C\{^1H\}$ NMR (50.31 MHz) **2**, C_5Me_5 (d, δ 139.7, J_{PC} = 14.7 Hz); C_5Me_5 (s, δ 11.5), **3**, C_5Me_5 (d, δ 137.8 J_{PC} = 13.4 Hz), C_5Me_5 (s, δ 12.6); ^1H NMR (90.0 MHz) **2**, C_5Me_5 (d, 15 H, δ 1.22, J_{PCCH} = 12.0 Hz), **3**, C_5Me_5 (d, 15 H, δ 2.16, J_{PCCH} = 3.0 Hz). These observations are consistent with the η^5 attachment of an RP^+ moiety to the Me_5C_5 ring or with fluxional system possessing lower degrees of hapticity. MNDO calculations[6] on the model cation $[C_5Me_5PMe]^+$ reveal that the global minimum corresponds to an η^2 structure:[7]



When CH_2Cl_2 solutions of **2** were allowed to stand ~5 days at room temperature, the NMR peaks of **2** disappeared gradually and were replaced by those of **5**. The ^{31}P chemical shift and P–H coupling constants of **5** (d, δ 87.1, J_{PH} = 503.6 Hz) are in the range anticipated[8] for phosphonium salts of type $[R_3PH]^+$, thus suggesting the formulation



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Confirmation of the above formulation is provided by $^{13}C\{^1H\}$ NMR (50.31 MHz) spectroscopy (−35 °C). A doublet at δ 58.0 (J_{PC} = 16.7 Hz) is attributable to the CH_2 group, and the four methyl resonances appear as singlets at δ 10.7, 11.5, 11.9, and 12.0. A large doublet at δ 60.9 (J_{PC} = 132.4 Hz) is assignable to the α ring carbon attached to phosphorus. The β ring carbons appear at δ 144.4 (d, J_{PCC} = 8.8 Hz) and 147.1 (d, J_{PCC} = 10.9 Hz), and the γ ring carbons appear at δ 129.7 and 132.7. Very similar observations were made when CH_2Cl_2 solutions of **3** were allowed to stand at ambient temperature. The rate of production of phosphonium salt **6** from **3** is slightly faster than the **2** → **5** rearrangement (^{31}P NMR (36.43 MHz) for **6**: (d, δ 72.2, J_{PH} = 565.7 Hz)). The conclusion that the P–H bonds in **5** and **6** do not arise from solvent was established by the fact that no P–D bond formation took place when the reactions were conducted in CD_2Cl_2. The products therefore arise from the intramolecular insertion of P^+ into a C–H bond of a Me_5C_5 methyl group. Finally, we draw attention to the striking parallel between our findings and the observation that the bis(pentamethylcyclopentadienyl) compounds of titanium and zirconium also undergo ring methyl to metal hydrogen shifts.[9,10]

Acknowledgment. Generous support from the National Science Foundation (Grant CHE-8205871) and the Robert A. Welch Foundation is gratefully acknowledged. Thanks are also due to Jon Lasch for the MNDO calculations and Dr. B. Shoulders for helpful discussions on NMR spectroscopy.

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[4] The $AlCl_4^-$ anion is characterized by a sharp resonance (w_h ~10–20 Hz) at δ ~103. See: Akitt, J. W. *Annu. Rep. NMR Spectrosc.* **1972**, *5A*, 465.

[5] The new chlorophosphine, $(Me_5C_5)[(Me_3Si)_2CH]PCl$ (**4**) was prepared by the action of $(Me_3Si)_2CHLi$ with $C_5Me_5PCl_2$ in Et_2O solution and characterized by high-resolution mass spectrometry: calcd for $C_{17}H_{34}Si_2PCl$ 360.1625, Found 360.1613.

[6] For MNDO parameters for phosphorus, see: Dewar, M. J. S.; McKee, M.; Rzepa, H. *J. Am. Chem. Soc.* **1978**, *100*, 3607 and references to earlier work cited therein.

[7] For carbocation analogues of this structure, see: (a) Swatton, D. W.; Hart, H. *J. Am. Chem. Soc.* **1967**, *89*, 5075. (b) Childs, R. F.; Winstein, S. *J. Am. Chem. Soc.* **1968**, *90*, 7146. We are indebted to a referee for bringing this work to our attention.

[8] See, for example: Mavel, G. *Annu. Rep. NMR Spectrosc.* **1973**, *5B*.

[9] Bercaw, J. E. *J. Am. Chem. Soc.* **1974**, *96*, 5087. Bercaw, J. E. *Adv. Chem. Ser.* **1978**, *No. 167*, 136.

[10] For related work on ethyl–tungsten compounds, see: Chong, K. S.; Green, M. L. H. *Organometallics* **1982**, *1*, 1586 and references therein.

β-Hydrogen Effects in Alkylalkoxides of Dimolybdenum (M≡M)

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The reaction of a metal alkyl to form a metal hydride and alkene and its reverse, alkene insertion into a metal hydride, are fundamental and important reactions in organo–transition-metal chemistry.[1,2] We here report observations of β-hydrogen effects at a dinuclear metal center that show rather unusual, if not unprecedented, features when compared to those well documented at mononuclear centers.

Addition of alcohols to hydrocarbon solutions of 1,2-$Mo_2R_2(NMe_2)_4$ compounds[3] yields either 1,2-$Mo_2R_2(OR')_4$ or $Mo_2R(OR')_5$ compounds according to eq 1 and 2.[4]

$$Mo_2R_2(NMe_2)_4 + 4R'OH \rightarrow Mo_2R_2(OR')_4 + 4HNMe_2 \quad (1)$$

R = Me, R' = *t*-Bu; R = CH_2CMe_3, CH_2SiMe_3, R' = *t*-Bu, *i*-Pr, *t*-CH_2Bu, Et

$$Mo_2R_2(NMe_2)_4 + 5R'OH \rightarrow Mo_2R(OR')_5 + RH + 4HNMe_2 \quad (2)$$

R = C_2H_5, C_3H_7, R' = *t*-Bu, *i*-Pr

In both eq 1 and 2, the rate of alcoholysis shows a marked dependence on the steric bulk of R and R'. Alcoholysis of the alkyl ligands, Mo–R + R'OH → MoOR' + RH, is slower than the alcoholysis of the amide ligands. The compounds $Mo_2Me_2(O\text{-}t\text{-}Bu)_4$ is coordinatively unsaturated and reacts with donor ligands. The compound $Mo_2Me_2(O\text{-}t\text{-}Bu)_4(py)_2$, where py = pyridine, has been characterized by a single-crystal X-ray study.[5]

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[1] Kochi, J. K. In "Organometallic Mechanisms and Catalysts"; Academic Press: New York, 1978.

[2] Parshall, G. W. In "Homogeneous Catalysis: The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes"; Wiley: New York, 1980.

[3] Chisholm, M. H.; Haitko, D. A.; Huffman, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 4046.

[4] All reactions were carried out in dry and oxygen-free solvents and atmospheres. The new compounds are yellow or orange solids which sublime and yield molecular ions in the mass spectrometer. Satisfactory elemental analyses have been obtained.

0002-7863/83/1505-2075$01.50/0