The molecular structure of $(\eta^6\text{-}C_6Me_6)Ta(DIPP)Et_2$[16,17] (3; Figure 2) reveals an interesting comparison to the parent chloride. Both structures feature a coordinated C_6Me_6 ligand which shows (i) substantial folding[18] (the dihedral angle between the C(1)–C(2)–C(3)–C(4) and C-(1)–C(2')–C(3')–C(4) planes in 3 is 27.3 (0.2)°, which compares with 26.8 (0.3)° for $(\eta^6\text{-}C_6Me_6)Ta(DIPP)Cl_2$[8]), (ii) an interruption of aromaticity within the C_6Me_6 ring (viz. a 1,4-diene type π localization), and (iii) the close approach of C(1) and C(4) to the metal (2.302 (5) and 2.187 (5) Å, respectively, compared to an average 2.481 (4) Å for the other arene carbons). These features may be attributed to a back-bonding interaction between filled metal δ functions and the arene LUMO.[8,15] In addition, the metal–carbon distances (C(1) vs C(4)) may reflect a structural trans effect since C(1) is "trans" to the strong π-donor alkoxide ligand. The rotational conformation of the arene ring in 3 is such that the ethyl Ta–C_α and alkoxide Ta–O–C_{ipso} linkages perfectly eclipse the arene carbon atoms, rather than stagger them as in $(\eta^6\text{-}C_6Me_6)Ta(DIPP)Cl_2$ (1).[8] Finally, the plane of the DIPP ligand is oriented perpendicular to the arene, 90° from the DIPP plane in 1.[8]

Because α- or β-H elimination/abstraction reactions did not lead to tuck-in complexes in the dialkyls,[5a] alkyl hydrides were prepared. $(\eta^6\text{-}C_6Me_6)Ta(DIPP)Cl_2$ reacts with *1 equiv* of CH_3CH_2MgBr (toluene, –60 °C) to provide the "double exchange" product $(\eta^6\text{-}C_6Me_6)Ta(DIPP)EtBr$ (5;

m/z = 628 (^{79}Br), 630 (^{81}Br)) in >95% yield (by ^{1}H NMR). This reaction is no doubt driven by the lattice energy of $MgCl_2$, as the expected product $(\eta^6\text{-}C_6Me_6)Ta(DIPP)EtCl$ is present in <5% yield. $(\eta^6\text{-}C_6Me_6)Ta(DIPP)EtBr$ (5) reacts with $LiBEt_3H$ (Et_2O, –65 °C) to provide $(\eta^6\text{-}C_6Me_6)Ta(DIPP)Et(H)$ (6) as an extremely soluble magenta solid in high yield (Scheme I). Similarly, $(\eta^6\text{-}C_6Me_6)Ta(DIPP)(CH_2SiMe_3)Cl$ (7; prepared from 1 and 1 equiv of $LiCH_2SiMe_3$) reacts smoothly with $LiBEt_3H$ under identical conditions to afford $(\eta^6\text{-}C_6Me_6)Ta(DIPP)(CH_2SiMe_3)(H)$ (8) as a purple solid. Both 6 and 8 exhibit a Ta*H* hydride resonance at ca. δ 5.87 (C_6D_6) and a ν(Ta–H) stretch between 1760 and 1780 cm^{-1}. While 8 is stable for months at room temperature in Et_2O, 6 decomposes slowly (to C_6Me_6 and unidentified products) over a period of hours.

The improved thermal stability of these alkyl complexes vs that of chloride complexes will allow a thorough PES characterization of their electronic structures, which has thus far not been possible for tantalum(III) arenes. Perhaps most significant is the electrochemical evidence for the formation and limited stability of a d^1 arene complex, an observation which supports their participation in the deoxygenative coupling of an acyl and a cyclopentadienyl ligand.[19] The isolation of such a complex with an appropriate counterion is an area of our continued research.

(16) Crystal data for $C_{28}H_{45}OTa$ (3): orthorhombic, *Pnma* (No. 62) (crystallographic mirror plane), a = 18.717 (4) Å, b = 12.487 (4) Å, c = 11.431 (3) Å, V = 2671.8 (11) Å^3, Z = 4, D(calc) = 1.44 g cm^{-3}, μ(Mo Kα) = 40.8 cm^{-1} (T = 23 ± 1 °C); 2811 total reflections (2456 unique), of which 2005 with $F_o^2 > 3.0\sigma(F_o^2)$ were included in the refinement. Hydrogen atoms were located (rotating anode source, 45 kV, 100 mA) and refined with B_{iso} = 5.0 Å^2; Lorentz and polarization corrections and an empirical absorption correction were applied to the data. Relative transmission coefficients ranged from 0.585 to 0.999 (average 0.789). Final R = 0.020, R_w = 0.027. The highest peak in the final difference Fourier was 0.42 e Å^{-3}.

(17) Selected bond lengths (Å) and angles (deg) for $(\eta^6\text{-}C_6Me_6)Ta$-(DIPP)Et$_2$ (3) (Bz* = C_6Me_6 centroid): Ta–C(1) = 2.302 (5), Ta–C(2) = 2.513 (3), Ta–C(3) = 2.448 (4), Ta–C(4) = 2.187 (5), Ta–C(10) = 2.207 (4), Ta–O(20) = 1.912 (3); Bz*–Ta–C(10) = 109.38 (9), Bz*–Ta–O(20) = 151.0 (1), C(10)–Ta–C(10') = 103.1 (1), O(20)–Ta–C(10) = 88.0 (1), Ta–O-(20)–C(21) = 177.4 (3), Ta–C(10)–C(11) = 113.1 (3), C(1)–Ta–O(20) = 170.9 (2).

(18) A summary of structurally characterized "bent arenes" appears in ref 8.

(19) A transient Ta(IV) arene complex, (arene)Ta(O)Cl$_2$, is a possible intermediate in this reaction. See: Meyer, T. Y.; Messerle, L. *J. Am. Chem. Soc.* **1990**, *112*, 4564.

Synthetic Routes to the First P-Metalated Phosphiranes: Synthesis and Structure of (η5-Cyclopentadienyl)dicarbonyl[2,2,3-tris(trimethylsilyl)-1λ3-phosphacyclopropyl]iron

Heike Brombach, Edgar Niecke,* and Martin Nieger

*Anorganisch-Chemisches Institut der Universität Bonn, Gerhard Domagk Strasse 1, D-5300 Bonn 1, FRG*

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Summary: Metallophosphiranes **2a–c** have been obtained by heterogeneous metalation of ClPCH(SiMe$_3$)C-(SiMe$_3$)$_2$ (1) or by reaction of the corresponding *P*-Me$_5$C$_5$-substituted phosphirane 4 with (CO)$_3$Mo(MeCN)$_3$ via a C$_5$Me$_5$ shift from phosphorus to the transition metal. One of the final products **2a** has been characterized by X-ray structure analysis.

The coordination chemistry of phosphorus-containing small ring systems is well established, and a vast number of such species, including saturated as well as unsaturated three-membered P/C-ring systems, are known.[1] Only recently this chemistry has been further expanded by in-

(1) Mathey, F. *Chem. Rev.* **1990**, *90*, 997 and references cited therein.

Scheme I

2a: R = H, M = Fe, (n = 2)

2b: R = Me, M = Fe, (n = 2)

2c: R = Me, M = Mo, (n =3)
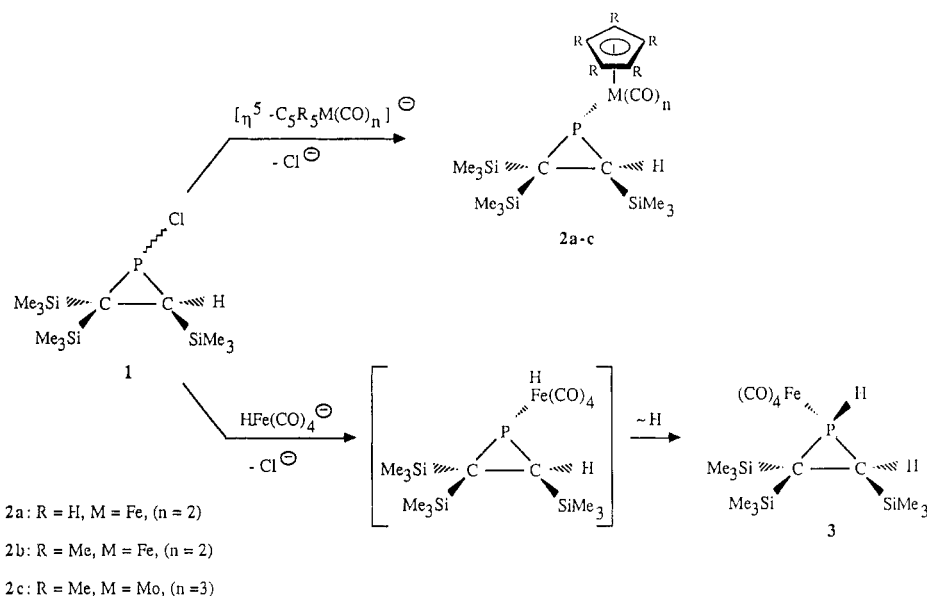
Scheme II
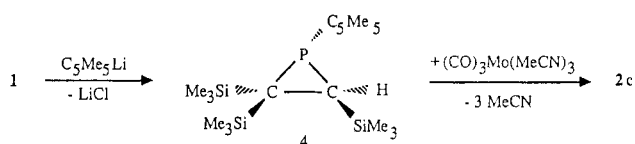
corporating organometallic substituents, in which the phosphorus atom acts as a one-electron donor.[2]

Here, we report on the metallophosphirane system (I), an until now unknown isomeric form of metallobis(methylene)phosphorane[3] (II), which has been shown to be suitable as a building block for phosphorus heterocycles.[3] A new type of the organometallic-substituted three-membered heterocycle 2 has been obtained by two different synthetic routes: (i) by heterogeneous metalation of the *P*-chlorophosphirane 1 or (ii) by reaction of the Me₅C₅-substituted phosphirane 4 with carbonyl complexes using the C₅Me₅ shift from phosphorus to the transition metal.

The reactions of 1 with 1 equiv of [(η⁵-C₅R₅)Fe(CO)₂]K (R = H, Me) or [(η⁵-C₅Me₅)Mo(CO)₃]K at −60 °C within 1–2 h (25 °C and heating at 40 °C for 3 h) yield deep red solutions of metalated λ³-phosphiranes 2a–c. Compounds 2a,b could be isolated as red crystals after evaporation of the solvent and recrystallization from a small amount of *n*-pentane (yield 50%, mp 104–106 °C (2a); 45%, mp 115–120 °C (2b)). Crude 2c remained after evaporation of all volatile material as a brown viscous oil. However, crystals of 2c could be obtained using the C₅Me₅-shift reaction by starting from the Me₅C₅-substituted λ³-phosphirane 4. This method has proven to be a convenient route to P-metalated 2-fold-coordinated phosphorus compounds.[4] (η¹-Me₅C₅)PCH(SiMe₃)C(SiMe₃)₂ (4) has been prepared from *P*-chlorophosphirane[5] 1 as follows: addition of 4 mmol of 1 in THF (5 mL) to a stirred THF (200 mL) suspension of K[C₅Me₅] within 4 h at 40 °C produces the λ³-phosphirane 4. The product was purified by evapora-

tion of the solvent, extraction of the residue with *n*-pentane, and recrystallization from diethyl ether. 4 was obtained in high yield (88%) as a colorless, thermally stable solid (mp 67–69 °C), and its structure could be deduced from the analytical and spectroscopic data.[6] The reaction of 4 with (MeCN)₃Mo(CO)₃ (THF, 40 °C, 1 h) produces a deeply colored solution, from which the product could be isolated after removing the volatiles and recrystallization of the residue from a small amount of *n*-pentane (yield 55–60%, mp 132–135 °C).

In contrast to the above-mentioned metalations, treatment of 3 mmol of 1 with [HFe(CO)₄]Na in 10 mL of ether yielded the λ³-phosphirane complex 3 instead of a metallophosphirane. The formation of this complex is proposed to proceed via a hydrogen shift from iron to the phosphorus atom of a transient metallophosphirane.

The λ³-phosphiranes 2a–c were characterized by elemental analysis, by mass, IR, and NMR (¹H, ¹³C, ³¹P)

(2) (a) Weber, U.; Lücke, E.; Boese, R. *Organometallics* **1988**, *7*, 978. (b) G. Bruder, Thesis, University of Bonn, 1989.

(3) Metternich, H.-J.; Niecke, E. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 312.

(4) Gudat, D.; Niecke, E.; Krebs, B.; Dartmann, M. *Chimia* **1985**, *39*, 277. Gudat, D.; Niecke, E.; *Organometallics* **1986**, *5*, 593. Gudat, D.; Niecke, E. *J. Chem. Soc., Chem. Commun.* **1987**, *10*. Jutzi, P.; Meyer, U. *Chem. Ber.* **1988**, *121*, 559.

(5) Niecke, E.; Leuer, M.; Nieger, M. *Chem. Ber.* **1989**, *122*, 453.

(6) Data for compounds 2a–c and NMR 4: MS, *m/e* (relative intensity) (EI, 70 eV); ¹H NMR, δ (C₆D₆); ¹³C{¹H} δ (C₆D₆); ³¹P{¹H} NMR, δ (C₆D₆); IR, cm⁻¹ (pentane). 2a: ³¹P{¹H}, −59.7 (s); ¹³C{¹H}, 216.2 (d, ²J_{PC} = 5.0 Hz, CO), 214.6 (d, ²J_{PC} = 4.7 Hz, CO), 86.3 (d, ²J_{PC} = 3.5 Hz, C₅H₅), 19.8 (d, ¹J_{PC} = 65.3 Hz, PC), 11.8 (d, ¹J_{PC} = 81.1 Hz, PC), 3.4 (d, ³J_{PC} = 12.3 Hz, SiCH₃), 2.2 (s, SiCH₃), 1.5 (d, ³J_{PC} = 3.7 Hz, SiCH₃); ¹H, 4.30 (s, 5 H, C₅H₅), 1.35 (d, ²J_{PH} = 3.0 Hz, 1 H, PCH), 0.38 (s, 18 H, SiCH₃), 0.34 (s, 9 H, SiCH₃); MS, 452 [<1, M⁺], 424 [4, M⁺ − CO], 396 [6, M⁺ − 2CO], 275 [7, M⁺ − CpFe(CO)₂], 73 [100, SiMe₃⁺]; IR, 2000 vs, 1955 s. Anal. Calcd for C₁₈H₃₃FeO₂PSi₃: C, 47.75; H, 7.35. Found: C, 47.68; H, 7.29. 2b: ³¹P{¹H}, −30.6 (s); ¹³C{¹H}, 217.5 (d, ²J_{PC} = 7.9 Hz, CO), 213.6 (d, ²J_{PC} = 3.8 Hz, CO), 98.7 (d, ²J_{PC} = 2.6 Hz, C₅Me₅), 19.6 (d, ¹J_{PC} = 65.9 Hz, PC), 12.8 (d, ¹J_{PC} = 72.8 Hz, PC), 10.3 (d, ³J = 8.6 Hz, C₅(CH₃)₅), 3.1 (d, ³J_{PC} = 10.1 Hz, SiCH₃), 2.4 (s, SiCH₃), 1.9 (d, ³J_{PC} = 3.1 Hz, SiCH₃); MS, 522 [<1, M⁺], 494 [6, M⁺ − CO], 466 [5, M⁺ − 2CO], 275 [9, M⁺ − Cp*Fe(CO)₂], 73 [100, SiMe₃⁺]; IR, 1985 vs, 1935 s; high-resolution mass spectrum (M⁺) calcd for C₂₃H₄₃FeO₂PSi₃ 522.1657, found 522.1650. 2c: ³¹P{¹H} −64.9 (s); ¹³C{¹H}, 239.5 (d, ²J_{PC} = 10.5 Hz, CO), 230.8 (d, ²J_{PC} = 7.5 Hz, CO), 229.6 (d, ²J_{PC} = 13.5 Hz, CO), 105.3 (s, C₅(CH₃)₅), 19.5 (d, ¹J_{PC} = 67.2 Hz, PC), 13.1 (d, ¹J_{PC} = 70.7 Hz, PC), 10.0 (d, ³J = 10.2 Hz, C₅(CH₃)₅), 2.9 (d, ³J_{PC} = 10.7 Hz, SiCH₃), 1.6 (d, ³J_{PC} = 3.5 Hz, SiCH₃), 1.5 (s, SiCH₃); ¹H, 1.60 [s, 15 H, C₅(CH₃)₅], 1.55 (d, ²J_{PH} = 1.8 Hz, 1 H, PCH), 0.39 (s, 9 H, SiCH₃), 0.36 (s, 9 H, SiCH₃), 0.32 (s, 9 H, SiCH₃); MS, 590 [<1, M⁺], 564 [9, M⁺ − CO], 536 [2, M⁺ − 2CO], 508 [4, M⁺ − 3CO], 275 [3, M⁺ − CpMo(CO)₃], 73 (100, SiMe₃⁺); IR, 1980 s, 1900 vs 1860 m. Anal. Calcd for C₂₄H₄₃MoO₃PSi₃: C, 48.77; H, 7.34. Found: C, 48.54; H, 7.30. 4: ³¹P{¹H}, −115.6 (s); ¹³C{¹H}, 163.8 [s, C₅(CH₃)₅], 135.8 [d, ¹J_{PC} = 60.4 Hz, C₅(CH₃)₅], 21.2 (d, ¹J_{PC} = 65.8 Hz, PC), 15.3 (d, ¹J_{PC} = 47.8 Hz, PC), 11.3 [s, C₅(CH₃)₅], 3.6 (d, ³J_{PC} = 4.4 Hz, SiCH₃), 2.1 (d, ³J_{PC} = 5.9 Hz, SiCH₃), 0.8 (s, SiCH₃); ¹H, 1.90 [s, 15 H, C₅(CH₃)₅], 1.31 (d, ²J_{PH} = 7.0 Hz, 1 H, PCH), 1.12 (d, ⁴J = 6.9 Hz, 9 H, SiCH₃), 0.35 (s, 9 H, SiCH₃), 0.32 (s, 9 H, SiCH₃); MS, 410 [21, M⁺], 275 [20, M⁺ − C₅(CH₃)₅], 136 [61, C₅(CH₃)₅H⁺], 135 [60, C₅(CH₃)₅⁺], 73 (100, SiMe₃⁺). Anal. Calcd for C₂₁H₄₃PSi₃: C, 61.38; H, 10.56. Found: C, 61.47; H, 10.50.
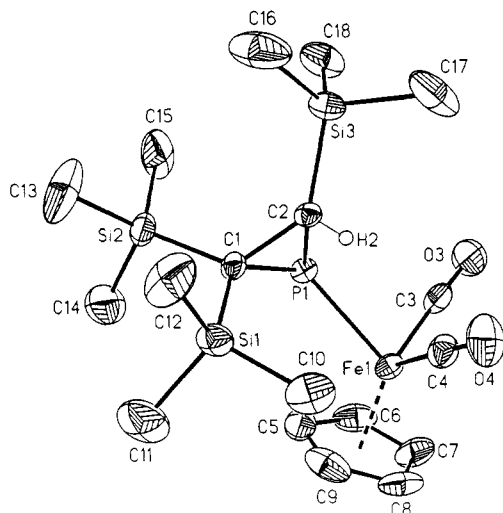
Figure 1. Structure of **2a**, showing one independent molecule and the atomic numbering scheme with ellipsoids at the 30% probability level. Important bond lengths (pm) and angles (deg) of **2a** (bond lengths and angles of the other molecule in the asymmetric unit are in brackets): P(1)-Fe(1) 233.1 (2) [234.5 (2)], P(1)-C(1) 187.2 (7) [188.6 (7)], P(1)-C(2) 186.1 (6) [185.6 (6)], C(1)-C(2) 155.4 (9) [156.5 (9)], C(1)-Si(1) 189.2 (8) [189.0 (8)], C(1)-Si(2) 189.9 (8) [191.2 (8)], C(2)-Si(3) 186.9 (7) [187.0 (7)]; Fe(1)-P(1)-C(1) 123.5 (2) [123.5 (3)], Fe(1)-P(1)-C(2) 117.6 (2) [116.0 (2)], C(1)-P(1)-C(2) 49.2 (3) [49.5 (3)], P(1)-C(1)-C(2) 65.0 (3) [64.3 (3)], P(1)-C(2)-C(1) 65.8 (3) [66.2 (3)].

spectra, and by a single-crystal determination of **2a**.[7] Compared with the $\delta(^{31}\text{P})$ values of a series of corresponding P-substituted phosphiranes, $\overline{\text{RPCH(SiMe}_3)\text{C}}$-(SiMe$_3$)$_2$ (δ -20.2 to -245.0),[5] the resonances of **2a-c** (δ

-59.7 (**2a**), -30.6 (**2b**), -64.9 (**2c**)) are observed in the "low field" range. This reflects a higher degree of s character of the phosphorus-carbon bonds, as is also shown by the large values for the coupling constants in **2a-c** (J_{PC} = 64-89 Hz) compared with corresponding organo-substituted derivatives.[5] The constitution of **3** was inferred from its mass spectrum[8] and ^{31}P NMR data. The presence of the second λ^3-phosphirane complex **3** is indicated by the characteristic high-field ^{31}P resonance with a doublet of doublets pattern (δ -119.2, $^1J_{\text{PH}}$ = 366.7 Hz, $^2J_{\text{PH}}$ = 5.2 Hz).

The structure of **2a** is illustrated in Figure 1. The P-C bonds (187 pm) in the triangle correspond to a bond order of unity, whereas the C-C distance (156 pm) is considerably lengthened. This results in a widening of the PCC angles (65°), whereas the CPC intracyclic angle is very small (49°). A similar bonding situation is observed for the λ^3-phosphirane $\overline{\text{PhPCPh}_2\text{C}}$(SiMe$_3$)$_2$.[9] However, in contrast to known λ^3-phosphiranes[1] the exocyclic angles at phosphorus are widened (120°) due to the presence of the bulky organometallic substituent. This indicates a high degree of s character in the Fe-P bond. The bond length itself (234 pm) is comparable to those in the P-metalated diphosphirane (η^5-C$_5$H$_5$)Fe(CO)$_2$PP(^{t}Bu)C(Ph)SiMe$_3$[2b] and 1,2-diphosphaspiro[2.2]pentane (η^5-C$_5$Me$_5$)Fe(CO)$_2$PP-(2,4,6-^{t}Bu$_3$C$_6$H$_2$)CCH$_2$CH$_2$.[2a]

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(7) Single crystals of **2a** were obtained by low-temperature crystallization from pentane. The data were collected at ambient temperature on a Nicolet R3m four-circle diffractometer (ω-scan mode, Mo Kα radiation, λ = 71.069 pm) and solved and refined with SHELXTL and SHELXTL-PLUS, respectively. Compound **2a**, C$_{18}$H$_{33}$FeO$_2$PSi$_3$, M_r = 452.5, crystallizes in space group $P2_1/n$ (No. 14), with a = 1466.8 (5) pm, b = 1774.7 (5) pm, c = 1912.3 (9) pm, β = 97.11 (4)°, V = 4.940 nm^3, Z = 8, D_{calc} = 1.22 g cm^{-3}, μ(Mo Kα) = 0.82 mm^{-1}, and $F(000)$ = 1920. A total of 6476 unique reflections were recorded, of which 2755 were considered as unobserved [$F < 4\sigma(F)$], leaving 3721 for solution and refinement (451 parameters). The final residuals were R = 0.059 and R_w = 0.054 with weighting scheme w^{-1} = $\sigma^2(F)$ + gF^2 (g = 0.0005). The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were localized by a difference electron density determination and refined using a "riding" model.

(8) MS (EI, 70 eV, m/e (relative intensity)): 444 (2, M$^+$), 416 (3, M$^+$ - CO), 388 (2, M$^+$ - 2CO), 360 (8, M$^+$ - 3CO), 322 (28 (M$^+$ - 4CO), 73 (100, SiMe$_3$).

(9) Appel, R.; Gaitzsch, T.; Knoch, F.; Lenz, G. *Chem. Ber.* **1986**, *119*, 1977.

Thermal Reaction of Chromium (Acyloxy)carbene Complexes: Synthesis of Enol Esters

Björn C. Söderberg* and Michael J. Turbeville

Department of Chemistry, University of South Alabama, Mobile, Alabama 36688

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Summary: Reaction of tetramethylammonium pentacarbonyl(1-oxyalkylidene)chromate(0) complexes with acyl chlorides at -40 °C followed by slow warming to ambient temperature affords exclusively or predominantly *Z* enol esters in moderate to good yield.

A number of synthetically useful reactions of alkoxy and amino Fischer carbenes, especially those of chromium, have been developed since their discovery almost 30 years ago. Compounds with a variety of structures such as cyclo-

Scheme I
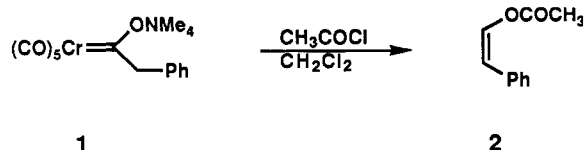
butanones, β-lactams, cyclopropanes, amino acids, and fused aromatic systems can be prepared by utilizing these reagents.[1]