Interaction of Phosphines Containing Cyclopropyl Substituents with Group 8 Metals

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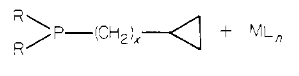
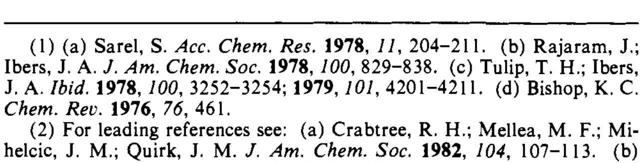
Metal centers react with cyclopropanes in a variety of ways.[1] For example, with Pt(0) or Pt(II) centers metallacycles are the usual products,[1b] whereas with Ir(I) centers allyl hydrides are occasionally formed.[1c] Both types of products are of current interest in connection with the metal-mediated transformations of organic substrates. In the reactions of metal centers with cyclopropanes there are no reports of C–H bond activation that leads to the cyclopropane ring being σ bound to the metal, although C–H activation in normal alkanes is known.[2] The C–H bonds of cyclopropane are thought to be as strong or stronger than those in normal alkanes.[3]

As part of our continuing interest in metallation reactions of cyclopropanes and of alkanes in general,[1b,1c] we have begun an examination of the interaction of metal centers with phosphine ligands that contain cyclopropyl substituents. In these systems we have varied the R groups on the phosphine (phenyl or *tert*-butyl), the number of methylene units between the phosphorus and the cyclopropane (0 or 1), and the group 8 metal centers.[4,5]



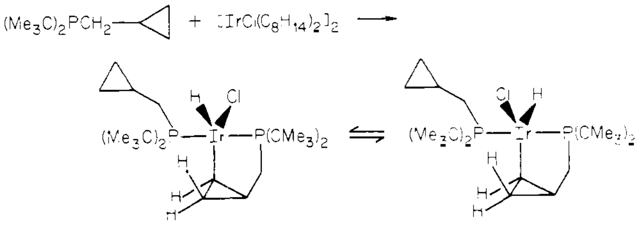
Here we describe some of the rich chemistry that occurs with di-*tert*-butyl(cyclopropylmethyl)phosphine and some group 8 metal centers. In so doing we demonstrate the C–H and C–C activation of the cyclopropyl ring, depending on the metal and solvent used. Both types of cyclopropyl activation occur preferentially over that in the *tert*-butyl ligand.[5]

The platinum complex *trans*-$PtCl_2((Me_3C)_2PCH_2(C_3H_5))_2$ (**1**)[6] is synthesized by combining the metal halide with 2 equiv of the phosphine in $MeOH/H_2O$ and stirring at room temperature for several days. Upon refluxing the resulting complex in 2-methoxyethanol for 2 h, one obtains cyclometalated material **2** with loss of HCl. The structure of **2** has been deduced from NMR spectroscopy and X-ray crystallography.[7] This is, to our knowledge, the first example of a σ allyl being isolated from the activation of a cyclopropane by a transition-metal complex.



1 2

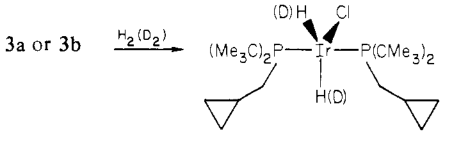
When di-*tert*-butyl(cyclopropylmethyl)phosphine reacts with $[IrCl(C_8H_{14})_2]_2$ in toluene, two diasteriomers containing five-coordinate Ir(III) are formed.[8,9] Their structures have been deduced from spectroscopic data and from their reaction chemistry.



3b 3a

In methylene chloride and other polar solvents these metallacyclopentanes undergo an isomerization to produce a single product. From spectroscopic data,[10] the formation of this product from both metallacyclopentanes, and its reaction chemistry, we suggest the product **4** could contain a metallacyclopentane ring fused to a cyclopropene ring. Further characterization of **4** awaits a crystal structure determination.

These five-coordinate, 16-electron Ir(III) complexes (**3a**, **3b**, and **4**) react rapidly with a number of small molecules, including COS, CS_2, CO, and H_2. With COS and CS_2 reductive elimination of the cyclopropane occurs. The expected six-coordinated adducts, with the metalated cyclopropane intact, are formed with CO. With H_2, product **5** is obtained for **3a** and **3b**.[11] Deuteration experiments suggest that reductive elimination of the cyclopropane occurs prior to reaction with D_2 or H_2. The formation of **5** is



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(4) These new phosphines have been synthesized by the established routes to phosphine ligands, i.e., (1) alkyl halide plus lithium phosphide, (2) alkyllithium plus chlorophosphine, or (3) secondary phosphine plus alkyl halide and subsequent treatment. See: (a) Kosolapoff, G. M., Maier, L., Eds. "Organic Phosphorus Compounds"; Wiley-Interscience: New York, Vol. 1, 1972. Diphenylcyclopropylphosphine and tricyclopropylphosphine have been prepared previously. (b) Cowley, A. H.; Mills, J. L. *J. Am. Chem. Soc.* **1969**, *91*, 2915–2919. (c) Denney, D. B.; Gross, F. J. *J. Org. Chem.* **1967**, *32*, 2445–2447.

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(6) Complex **1**: IR (Nujol mull) ν_{PtCl} 328 (s) cm^{-1}; ^1H NMR (C_6D_6, 270 MHz) δ 0.38 (m, cyclopropyl), 0.59 (m, cyclopropyl), 1.37 (m, cyclopropyl), 1.52 (t, J = 6 Hz, methyl), 2.07 (m, CH_2); $^{13}C\{^1H\}$ NMR (C_6D_6, 67.80 MHz) δ 8.76 (d, J = 2 Hz, C_3H_5), 30.94 (s, CH_3), 36.25 (t, J = 11 Hz); $^{31}P\{^1H\}$ NMR (C_6D_6, 109.16 MHz) δ 19.54 (PtP, J = 2465.8 Hz). Anal. Calcd for $C_{24}H_{50}P_2PtCl$: C, 43.24; H, 7.56. Found: C, 43.66; H, 7.58.

(7) Complex **2**: IR (Nujol mull) $\nu_{C=C}$ 1615, ν_{PtCl} 257 (s) cm^{-1}; ^1H NMR (C_6D_6, 270 MHz) δ 0.35–0.60 (m, cyclopropyl), 1.413 (t, CH_3, J = 13.6 Hz), 1.97 (PCH_2) 2.06 (s, allylic CH_3), 2.78 (m, $PtCH_2$), 5.33 (m, vinyl H); $^{31}P\{^1H\}$ NMR (C_6D_6, 109.16 MHz) **2a** δ 72.43 (PtP J = 2991.6 Hz), 45.28 (PtP, J = 2834.3 Hz), (PP, J = 403.4 Hz), **2b** 69.30 (PtP, J = 3080.5 Hz), 43.00 (PtP, J = 2776.2 Hz), (PP, J = 401.7 Hz). Anal. Calcd for $C_{24}H_{49}P_2PtCl$: C, 45.75; H, 7.84; Cl, 5.63. Found: C, 45.08; H, 7.52; Cl, 5.69. ^{31}P NMR spectroscopy indicates the presence of two conformational isomers in solution. Crystallographic data: space group, C_{2h}^5-$P2_1/c$; a = 11.847 (5) Å, b = 15.451 (7) Å, c = 16.802 (8), β = 116.70 (2)°, Z = 4. R_F = 0.044, R_{wF} = 0.047 based on 4630 reflections ($F_o^2 > 3\sigma(F_o^2)$).

(8) Complexes **3a** + **3b**: IR (Nujol mull) ν_{IrH} 2300, ν_{IrCl} 245 cm^{-1}; ^1H NMR (C_7D_8, 270 MHz) δ −44.8 (t, $^2J_{HP_{cis}}$ = 13.2 Hz, IrH, **3a**), −42.0 (t, $^2J_{HP_{cis}}$ = 12.6 Hz, IrH, **3b**), complex cyclopropyl and *tert*-butyl regions; $^{31}P\{^1H\}$ NMR (C_7D_8, 109.16 MHz) δ 94.4, 38.2 (dd, $^2J_{PP_{trans}}$ = 366.3 Hz, **3a**), 88.5, 38.3, (dd, $^2J_{PP_{trans}}$ = 360.5 Hz, **3b**). Anal. Calcd for $C_{24}H_{50}P_2IrCl$: C, 45.88; H, 8.02. Found: C, 45.72; H, 7.90.

(9) Another example of an Ir(III)–σ-cyclopropyl complex is $IrCl_2(C_3H_5)(CO)(PMePh_2)_2$ (Jones, N. L.; Ibers, J. A. *Organometallics*, in press).

(10) Complex **4**: IR (Nujol mull) ν_{IrH} 2305, 1928, ν_{IrCl} 255 cm^{-1}; ^1H NMR (C_7D_8, 270 MHz) δ −40.7 (t, $^2J_{HP_{cis}}$ = 13.9 Hz, IrH), 0.06 (s), 0.28, 0.49, 0.84 (m, cyclopropyl), 1.05 (d, $^3J_{HP}$ = 12.5 Hz, cyclopropyl), 1.29 (d, $^3J_{HP}$ = 11.7 Hz, CCH_3), 1.31 (d, $^3J_{HP}$ = 12.7 Hz, CCH_3), 1.37 (d, $^3J_{HP}$ = 12.2 Hz, CCH_3), 1.48 (d, $^3J_{HP}$ = 12.5 Hz, CCH_3), 1.93 (s), 2.11 (m), 2.22 (d, J_{HP} = 7.3 Hz), 6.47 (d, J_{HP} = 7.3 Hz); $^{13}C\{^1H\}$ ($CDCl_3$, 67.8 MHz) δ 7.06 + 7.96 (s, cyclopropyl), 22.53 (d, J = 22.0 Hz), 23.80 (d, J = 14.7 Hz), 29.53, 30.28, 30.64, 31.29 (s, CCH_3), 32.01 (d, J = 29.3 Hz), 34.57 (d, J = 19.5 Hz), 36.45 (d, J = 17.1 Hz), 37.55 (d, J = 14.7 Hz), 119.6 (s), 143.91 (d, J = 14.6 Hz); $^{31}P\{^1H\}$ (C_7D_8, 109.16 MHz) δ 66.7, 38.7 (dd, $^2J_{PP_{trans}}$ = 351.7). Anal. Calcd for $C_{24}H_{50}P_2IrCl$: C, 45.88; H, 8.02. Found: C, 45.70; H, 7.88.

(11) Complex **5**: IR (Nujol mull) ν_{IrH} 2245, 2295 cm^{-1} (ν_{IrD} 1612, 1653 cm^{-1}); ^1H NMR (C_7D_8, 270 MHz) δ −32.19 (t, $^2J_{HP_{cis}}$ = 13 Hz), 0.35 (m, cyclopropyl), 0.51 (m, cyclopropyl), 1.32 (t, $^3J_{HP}$ = 6.2 Hz, CH_3), 2.09 (m, CH_2); ^{31}P NMR (C_7D_8, 109.16 MHz) δ 55.80(s). Anal. Calcd for $C_{24}H_{52}P_2IrCl$: C, 45.74; H, 8.31. Found: C, 45.86; H, 7.85.

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additional evidence that the cyclopropane rings are intact in **3a** or **3b**.

Irradiation of **3a** or **3b** in protonated solvents also results in the formation of **5**. In deuterated solvents (C_7D_8, C_6D_6, or C_6D_{12}) photolysis results in the formation of the deuteride hydride, $IrClHD[P(H_2C(C_3H_5))(CMe_3)_2]_2$, perhaps by homolysis of the Ir–C bond with consequent formation of radicals that pick up deuterium from the solvent.

We are currently investigating the reactions of other cyclopropyl phosphines with group 8 metals and the further reactions of the five-coordinate, 16-electron iridium(III) compounds reported here.

Acknowledgment. This work was kindly supported by the National Science Foundation (CHE80-09671).

Registry No. **1**, 84081-80-1; **2**, 84081-81-2; **3a**, 84129-17-9; **3b**, 84081-82-3; **4**, 84081-83-4; **5**, 84081-84-5; $[IrCl(C_8H_{14})_2]_2$, 12246-51-4; $IrClHD[P(H_2C(C_3H_5))(CMe_3)_2]_2$, 84081-85-6.

Synthesis of Carbene Complexes of Group 4 Metals from Alkylidene-Bridged Heterobimetallic Precursors

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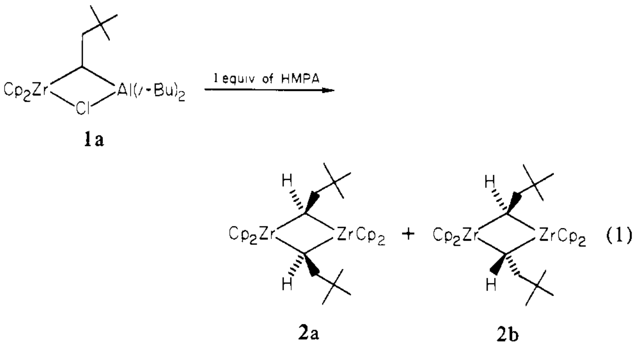
In contrast to carbene complexes of groups 5[1] and 6[2] metals, which have been extensively studied, knowledge of carbene complexes of group 4 metals is limited to one observed Zr species[3] and several postulated Ti intermediates.[4,5] This relative lack of information may be due to limitations in synthetic techniques heretofore available and not to any inherent instability of members of this class.

When zirconium complex **1a**[6] is treated with 1 equiv of hexamethylphosphoramide (**warning**: cancer suspect; a good ligand for aluminum complexes[7]), red-brown crystals can be isolated (31% yield) whose ^1H NMR spectrum[8] suggests it to be a mixture of carbene dimerization products **2a** and **2b** (3:1).[9] We reasoned that if a bridged alkylidene complex were treated with HMPA *in the presence of another ligand that would strongly coordinate the transition-metal carbene complex* thus formed, the latter species might possess sufficient stability to enable its direct observation and examination in subsequent reactions. Thus, when a solution of, for example, **1a** and triphenylphosphine (which should be a good ligand for Zr(II)[10]) is treated with 1 equiv of HMPA (toluene, –40 °C) and is allowed to warm to room temperature over a period of 15 min, a mixture is obtained whose ^1H HMR spectrum is consistent with the formation of carbene complex **3a**, which could be purified[11] as a yellow-orange oil by concentrating the toluene solution, adding pentane, cooling to –78 °C, removing the pentane supernatant from the precipitate formed, and evaporating the solvent. Proton NMR analysis of the pentane-soluble oil showed it to be **3a**[12] and the precipitate to be **4**. A similar procedure gives $Cp_2Ti(CH_2)(PEt_3)$, **5** (Cp = cyclopentadienyl). For **1a**, small amounts of three other Cp-containing products are noted.[13] Two of these are the dimers **2a** and **2b**. The third becomes the major Cp-containing product when a reaction, similar to the one described above, is carried out with 2 equiv of HMPA and no other organophosphine. On the basis of ^1H and ^{31}P NMR studies, its structure is assigned to be **3a″**.



3:1 yield

Low-temperature ^1H and ^{31}P NMR analysis shows that HMPA forms a complex with **1a** on mixing at –30 °C. Signals for carbene complex **3a** appear in the presence of PPh_3 slowly at –10 °C; at +10 °C the reaction is complete within 1 h. The titanium system is more reactive; activation of **2** by HMPA in the presence of triethylphosphine gives the corresponding titanium complex (**5**) on mixing at –30 °C.

Yields vary for formation of carbene complexes **3** as a function of trapping phosphine ligand used (see Table III).[14] In general, strong σ-donor phosphines of small cone angle[15] are favored for complexation relative to HMPA and for increasing thermal stability of the carbene species. For **3a′** the half-life for decomposition (at room temperature in solution) is ca. 1 week, for **3a** several days, and for the HMPA complex **3a″** several hours.

As the alkylidene unit of **1** becomes sterically *less* crowded, *lower* yields of carbene complexes are obtained by reaction with HMPA and a phosphine. Cyclohexanone treatment of the reaction mixtures obtained from **1e** gives, on hydrolysis, a significant amount of cyclohexanol (37% based on **1e**), and analysis of the reaction mixture prior to hydrolysis also showed the presence of a neohexenylzirconium species. These facts infer that β-H elimination occurs to give an aluminum hydride (in reversal of the synthesis procedure for **1**);[5] this process may compete with carbene complex formation. In this way, reaction partitioning might depend on substitution at the γ position of the alkyl chain, reflecting the ease of attainment of a preferred dihedral angular relationship between a β C–H bond and the α Al–C bond:[16] bulky

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(8) NMR spectra were recorded in toluene-d_8. ^{31}P NMR shifts are referenced to external H_3PO_4 (positive to low field).

(9) Hydrolysis of the **2a**–**2b** mixture gave cyclopentadiene and 3,3-dimethylbutane as the sole organic products.

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(11) We thank Professor R. H. Grubbs for suggesting this type of purification scheme.

(12) H–P coupling constant data are inconsistent with an ylide structure (see ref 3).

(13) These were carried through the purification procedure in small amount with the carbene complex.

(14) Yields for the formation of other neohexylidene zirconocene complexes include $PMePh_2$ (63%), $P(p\text{-}C_6H_4OMe)_3$ (64%), and $P(p\text{-}C_6H_4F)_3$ (37%).

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