Triflic Acid Mediated Ligand Fragmentation. Transfer of an Isopropyl Group from Triisopropyl Phosphite to Iridium

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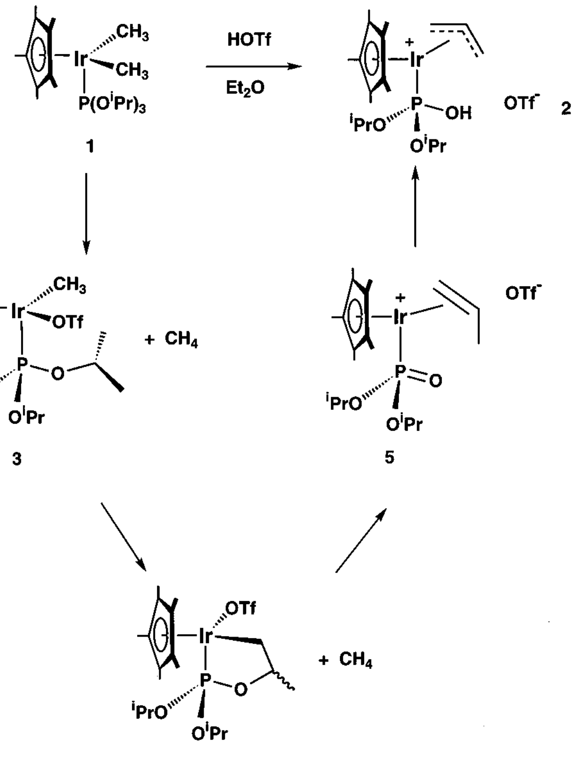
*Summary: Trifluoromethanesulfonic acid (HOTf) reacts with $Cp^*Ir(P(O^iPr)_3)(CH_3)_2$ to form methane and the allyl complex $[Cp^*Ir(\eta^3\text{-}C_3H_5)(P(OH)(O^iPr)_2)]OTf$ (**2**). Mechanistic studies show that the phosphite dealkylation is preceeded by protonation of an Ir−C bond to give $Cp^*Ir(CH_3)OTf(P(O^iPr)_3)$, then cyclometalation of the ligand, resulting in a pair of diastereomeric metallacyles which decompose to give **2**.*

Scheme 1



Complexes bearing phosphite ligands are employed in a variety of metal catalyzed processes such as hydrogenation, hydroformylation, and hydrocyanation.[1] Usually these catalysts are more reactive than analogous systems bearing phosphine ligands, but the phosphite complexes are more susceptible to degradation by routes such as hydrolytic cleavage of the C−O bonds[2] and Arbuzov-type dealkylation reactions.[3] This communication describes an unusual acid-mediated dealkylation reaction in which an isopropyl group is transferred from a phosphite ligand to an iridium center. Most noteworthy is that dealkylation of the ligand occurs *after* the added acid is consumed. This is quite different from the previously described mechanisms for phosphite decomposition.[3]

The triisopropyl phosphite substituted complex $Cp^*Ir(P(O^iPr)_3)(CH_3)_2$ (**1**, $Cp^* = \eta^5\text{-}C_5Me_5$) was prepared in analogy to the known PPh_3 and PMe_3 substituted systems.[4] Addition of 1.0 equiv of HOTf ($OTf = CF_3SO_3$) to an ether solution of **1** resulted in gas evolution; however, the isolated product has spectral properties which were quite different from several previously prepared $Cp^*Ir(L)(CH_3)X$ complexes.[4,5] On the basis of the spectral and analytical data, the product is assigned as $[Cp^*Ir(\eta^3\text{-}C_3H_5)(P(OH)(O^iPr)_2)]OTf$ (**2**, Scheme 1). The formation of an η^3-allyl group is confirmed by a DEPT 135 experiment, which shows a single methylene carbon at δ 37.4 ppm ($J_{CH} = 166.5$ Hz) and a methine carbon at δ 76.8 ppm ($J_{CH} = 166.2$ Hz). A broad singlet in the ^1H NMR spectrum at δ 10.8 ppm, which disappears when the sample is treated with D_2O, is characteristic of a hydrogen-bonded hydroxyl group. The $^{31}P\{^1H\}$ NMR signal shifts upfield from a value of δ 84.5 ppm in the starting dimethyl complex to 61.4 ppm in **2**, a trend commonly observed upon dealkylation of a phosphite ligand.[3] This compound may be prepared independently by addition of AgOTf and $(^iPrO)_2P(O)H$ to a CH_2Cl_2 solution of $Cp^*Ir(\eta^3\text{-}C_3H_5)Cl$.[6,7]

Labeling studies were used to trace the origins and fates of the protons and alkyl groups during the reaction. The product produced from addition of DOTf to an $Et_2O\text{-}d_{10}$ solution of $Cp^*Ir(CD_3)_2(P(O^iPr)_3)$ is identical to samples of **2** formed from the reaction of the nondeuterated compounds. Most notable is the formation of the $(^iPrO)_2PO\mathit{H}$ ligand. No deuterium incorporation into the complex was observed by ^2H NMR. The only significant deuterium-containing species observed was CD_4.[8] The fate of the iridium−methyl groups was determined by $^{13}C\{^1H\}$ and ^1H NMR spectroscopies. When $Cp^*Ir(^{13}CH_3)_2(P(O^iPr)_3)$ was treated with DOTf, a 1:1 mixture of $^{13}CH_4$ and $^{13}CH_3D$ was observed. These data suggest that of the two protons lost from an

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[1] Babin, J. E.; Whitaker, G. T. U.S. Patent 5,491,266, 1996.

[2] Babin, J. E.; Maher, J. M.; Billig, E. U.S. Patent 5,364,950, 1992.

[3] For a review article on phosphite dealkylations reactions see: Brill, T. B.; Landon, S. J. *Chem. Rev.* **1984**, *84,* 577−585.

[4] Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108,* 1537−1550.

[5] Burger, P.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115,* 10462−10463.

[6] McGhee, W. G.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110,* 4246−4262.

[7] The P(III) tautomer of dialkyl phosphites may be trapped by unsaturated metal centers. See: Dalla Riva Toma, J. M.; Bergstrom, D. E. *J. Org. Chem.* **1994**, *59,* 2418−2422.

[8] The resolution of the spectrum was not sufficient to confirm the formation of CHD_3. A 1:1 mixture of CH_4 and CH_3D is formed upon addition of DOTf to **1**.

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isopropyl group, one is transferred to an iridium−methyl group, which leaves as methane, while the second is donated to the $(^{i}PrO)_2POH$ ligand.

Several intermediates are observed when the reaction is monitored by low-temperature NMR spectroscopy (see Scheme 1). Addition of 1.0 equiv of HOTf to an Et_2O-d_{10} solution of **1** at −100 °C resulted in rapid formation of methane and a new phosphite-containing product characterized by ^1H NMR signals at δ 1.70 and 1.48 ppm (d, $J_{PH} = 4.2$ Hz) in a ~5:1 ratio. The spectral data are consistent with the formation of the methyl−triflato complex $[Cp^*Ir(P(O^iPr)_3)(CH_3)]OTf$, **3**. Compound **3** is extremely reactive; after 10 min at −100 °C, some conversion to the allyl complex **2** and two additional Cp*-containing products **4** and **4a** (in a ~3:1 ratio) are observed. As the temperature of the sample is raised to −50 °C, complete conversion of **3** to **4**, **4a**, and **2** occurs. The intensity of the methane signal continues to increase during the course of the reaction. To further identify the structures of **4** and **4a**, a COSY spectrum was run. Complete analysis of the spectrum was not possible due to multiple overlapping resonances, but it did confirm the presence of two independent ABX spin systems. The $^{31}P\{^1H\}$ NMR spectrum at this temperature consists of two signals at δ 112.5 and 110.6 ppm in a 1:3 ratio, as well as the expected signal for **2**. These intermediates cleanly convert to **2** as the temperature is raised; no additional intermediates are observed.[9]

It is difficult to unambiguously assign the structures of these intermediates, but the spectral data are consistent with the formation of a diastereomeric pair of metallacycles, **4** and **4a**, formed by cyclometalation of the triisopropylphosphite ligand. The large downfield shifts observed in the $^{31}P\{^1H\}$ NMR spectrum of **4** give further support for the formation of metallacycles as intermediates. Orthometalation of triphenylphosphite, forming a five-membered chelate, produces a large downfield shift in the ^{31}P chemical shift.[10] This downfield shift is opposite the trend observed when a phosphite ligand is dealkylated.[3] The final product may form by C−O cleavage to give a cationic propylene complex **5**, which is then rapidly deprotonated by the metallophosphite ligand (Scheme 1) affording the final allyl complex.

The facility of the dealkylation reaction, especially considering the poor nucleophilicity[11] of the triflate anion, and the transfer of the isopropyl group to the iridium center are most unusual.[12] Classically, dealkylation reactions are promoted by the addition of a strong nucleophile such as I^- or CN^- to a cationic metal center[3] or protonation of a coordinated phosphite's oxygen with a strong acid.[13] The study shows that this acid-mediated phosphite dealkylation reaction occurs by a mechanism quite different from those previously described.[12−14] The work by Bergman and Burger[5] on intermolecular C−H activation reactions by $[Cp^*Ir(P(CH_3)_3)(CH_3)]OTf$ supports the proposed mechanism involving ligand metalation. It is not surprising that the bulky triisopropyl phosphite ligand would undergo intramolecular C−H activation.[15] This postulate is supported by the following observations: (1) CHD_3 forms from the reaction of $Cp^*Ir(CD_3)_2(P(O^iPr)_3)$ with DOTf, demonstrating that a ligand on the iridium complex donates a proton; (2) no dealkylation is observed when an iridium center that does not perform C−H activation reactions is formed from the added acid.[5,16] It is not clear why the C−O bond cleaves so readily, but formation of the η^3-allyl ligand undoubtedly provides a driving force for the fragmentation.[17]

Acid-mediated phosphite dealkylation is recognized as a common side reaction which can occur when these ligands are employed in catalysis. This study demonstrates that in certain instances, dealkylation may be promoted by intramolecular reactions of the ligand with a Lewis acidic metal center. Superficially the transformation is similar to classical phosphite dealkylation reactions yet the mechanism is quite different. It depicts yet another manner in which these versatile yet fragile ligands may decompose.

Experimental Section

General. Unless otherwise stated, all manipulations were conducted using standard Schlenk-line and glovebox techniques. Diethyl ether, hexane, and toluene were distilled from sodium/benzophenone; methylene chloride and acetonitrile were distilled from CaH_2. C_6D_6, THF-d_8, and Et_2O-d_{10} were vacuum transferred from sodium/benzophenone. Zinc chloride was dried by refluxing overnight in $SOCl_2$ and then heating to 100 °C *in vacuo*. All other reagents were used as received from standard chemical suppliers. The complex $[Cp^*IrCl_2]_2$ was prepared by the method of Maitlis.[18] ^1H, ^{31}P, and $^{13}C\{^1H\}$ NMR spectra were recorded at ambient temperature at 300.2, 121.8, and 75.71 MHz, respectively.

$Cp^*IrCl_2(P(O^iPr)_3)$. A 100 mL round bottom flask was charged with 380 mg (0.477 mmol) of $[Cp^*IrCl_2]_2$ and 30 mL of CH_2Cl_2. $P(O^iPr)_3$ (264 μL, 223 mg, 2.25 equiv) was added via syringe to the solution. After the mixture was stirred for 3 h at ambient temperature, the volatile materials were removed *in vacuo*. The bright orange solid was collected on a frit and washed with cold (−78 °C) hexanes. Residual solvent was removed *in vacuo* to afford 538 mg (93%) of analytically pure $Cp^*IrCl_2(P(O^iPr)_3)$. ^1H NMR (C_6D_6): δ 5.17 (m, 3H), 1.44 (d, $J = 3.2$ Hz, 15H), 1.23 (d, $J = 6.2$ Hz, 18H) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 93.3 (d, $J_{PC} = 3.9$ Hz), 71.2 (d, $J_{PC} = 7.0$ Hz), 24.2, 8.56 ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 72.7 ppm. IR(KBr): 2976 (m), 2871 (m), 1450 (m), 1020 (s), 983 (m), 764 (m) cm^{-1}. Anal. Calcd for $C_{19}H_{36}Cl_2IrCl_2O_3P$: C, 37.62; H, 5.98. Found: C, 37.39; H, 7.65.

$Cp^*Ir(CH_3)_2(P(O^iPr)_3)$ (1). A solution of 550 mg (0.907 mmol) of $Cp^*IrCl_2(P(O^iPr)_3)$ in 50 mL of THF was allowed to

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[9] The intermediates **4** and **4a** are also observed when HOTf is added to Et_2O-d_{10} solution of **2** at room temperature.

[10] Stewart, J. R. P.; Isbrandt, L. R.; Benedict, J. J. *Inorg. Chem.* **1976**, *15*, 2011−2013.

[11] The methyltrimethoxyphosphonium ion is stable as a triflate salt, while it has a fleeting existence in the presence of halides. Colle, K. S.; Lewis, E. S. *J. Org. Chem.* **1978**, *43*, 571−574.

[12] Thermolysis of $Ru[P(OMe)_3]_5$ at 120 °C produces $Ru[P(OMe)_3]_4(CH_3)[P(O)(OMe)_2]$. The mechanism of this rearrangement is not known. Alex, R. F.; Pomeroy, R. K. *Organometallics* **1982**, *1*, 453−459.

[13] Solar, J. M.; Rogers, R. D.; Mason, W. R. *Inorg. Chem.* **1984**, *23*, 373−377.

[14] Muetterties, E. L.; Kirner, J. F.; Evans, W. J.; Watson, P. L.; Ardel-Meguid, S. A.; Tavanaiepour, I.; Day, V. W. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 1056−1059.

[15] Cationic iridium complexes undergo facile cyclometalation of triphenylphosphine ligands. Diversi, P.; Iacoponi, S.; Ingrosso, G.; Laschi, F.; Lucherini, A.; Pinzino, C.; Uccello-Barretta, G.; Zanello, P. *Organometallics* **1995**, *14*, 3275−3287.

[16] Addition of acids of more strongly coordinating anions (HCl, CH_3CO_2H) to **1** results in good yields of the expected $Cp^*Ir(CH_3)X(P(O^iPr)_3)$ complexes. No reaction is observed upon addition of HOTf to an Et_2O solution of $Cp^*IrCl_2(P(O^iPr)_3)$.

[17] There are numerous examples of the formation of an η^3-allyl complex by deprotonation of a coordinated olefin. See: Trost, B. M.; Strege, P. E.; Weker, L.; Fullerton, T. J.; Dietsch, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3407−3415.

[18] White, C.; Yates, A.; Maitlis, P. M. In *Inorganic Syntheses*; Grimes, R., Ed.; John Wiley & Sons: New York, 1992; Vol. 29, pp 228−234.

stir at ambient temperature. CH_3Li (1.9 mL of a 1.4 M soltion in Et_2O, 2.7 mmol, 3.0 equiv) was added via syringe, resulting in color changes from yellow orange to brown and finally pale yellow. The solvent was removed under reduced pressure, and the yellow residue was extracted with hexanes (3 × 30 mL). The combined hexane extracts were filtered through a pad of Al_2O_3 supported on a frit. The filter cake was washed with an additional 30 mL of hexanes, and the solution was evaporated to yield an off-white solid. This was extracted into ~20 mL of hot acetonitrile. The resulting solution was filtered through fine frit while hot and cooled to −30 °C for 2 days. The resulting white crystals were collected on a frit and washed with ~3 mL of cold (−30 °C) acetonitrile. Residual solvent was removed *in vacuo* to afford 340 mg (66%) of analytically pure **2**. ^1H NMR (C_6D_6): δ 4.46 (m, 3H), 1.67 (d, J = 2.6 Hz, 15H), 1.22 (d, J = 6.2 Hz, 18H), 0.60 (d, J = 3.6 Hz, 6H) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 92.9 (d, J_{PC} = 4.9 Hz), 67.7 (d, J_{PC} = 4.7 Hz), 24.45 (d, J_{PC} = 4.1 Hz), 8.75, −24.32 (d, J_{PC} = 13.1 Hz) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 83.9 ppm. IR-(KBr): 2970 (m), 2812 (m), 1379 (m), 1004 (s), 970 (s), 880 (m), 761 (m) cm^{-1}. Anal. Calcd for $C_{21}H_{42}IrO_3P$: C, 44.58; H, 7.48. Found: C, 44.56; H, 7.65.

Cp*Ir($^{13}CH_3$)$_2$(P(O^{i}Pr)$_3$) (1-^{13}C). In the drybox, an oven-dried ampule attached to a Kontes high-vacuum stopcock was charged with 125 μL (281 mg, 2.0 mmol) of $^{13}CH_3I$, 20 mL of Et_2O, and ~100 mg of magnesium turnings, then closed and allowed to stir overnight at ambient temperature. $ZnCl_2$ (136 mg, 1.0 mmol) was added to the reaction mixture. After the mixture was stirred an additional 2 h at ambient temperature, the $ZnCl_2$ dissolved to give a biphasic solution. The ampule was removed from the drybox, atttached to a vacuum line, and degassed by three freeze−pump−thaw cycles. A similar ampule containing 350 mg (0.597 mmol) of Cp*IrCl$_2$(P(O^{i}Pr)$_3$) in 20 mL of toluene was degassed by the above procedure. The solution of ($^{13}CH_3$)$_2$Zn was then condensed onto the frozen toluene solution at −196 °C. The receiving flask was allowed to warm to room temperature and stir overnight. During this time, the color of the solution changed from bright orange to colorless. The volatile materials were removed *in vacuo*, and the residue was extracted with 3 × 15 mL hexane, filtered through a pad of Celite, and evaporated. Crystallization from acetonitrile afforded 227 mg (64% yield) of Cp*Ir($^{13}CH_3$)$_2$(P(O^i-Pr)$_3$). The use of ($^{13}CH_3$)$_2$Zn gave much higher yields of **1-^{13}C** than the above procedure using methyllithium or the corresponding Grignard reagent. Presumably, the presence of iodide interferes with the alkylation reaction. ^{13}C NMR (C_6D_6): δ −24.27 (d of q, J_{CH} = 127.3 Hz, J_{PC} = 13.1 Hz) ppm.

[Cp*Ir(η^3-C$_3$H$_5$)(P(OH)(O^{i}Pr)$_2$)]$^+$OTf$^-$ (2). Addition of HOTf (44 μL, 0.497 mmol, 0.95 equiv) to an Et_2O solution of **1** (296 mg, 0.523 mmol) resulted in a rapid color change from very pale yellow to bright orange. As the reaction mixture was allowed to stir at room temperature for 30 min, the color of the reaction medium faded, producing a colorless solution. The solvent was removed, and the pale yellow residue was washed with hexanes (2 × 10 mL), extracted into a miminum amount of hot Et_2O (~15 mL), and cooled to −30 °C. After 2 days, white crystals (300 mg, 84%) of analytically pure **2** were collected. ^1H NMR (THF-d_8): δ 10.8 (bs, 1H), 4.74 (m, 2H), 3.72 (m, 1H), 3.64, (m, 1H), 3.01 (d of d, J = 1.0 Hz, 6.7, 2H), 2.38 (m, 2H), 2.00 (d, J = 2.7 Hz, 15H), 1.30 (d, J = 6.1 Hz, 6H), 1.29 (d, J = 6.1 Hz, 6H) ppm. ^{13}C NMR (THF-d_8): δ 98.0 (d, J_{PC} = 2.5 Hz), 76.9 (d, J_{CH} = 166.3 Hz), 71.9 (d of d, J_{PC} = 9.4 Hz, J_{CH} = 148.2 Hz), 37.4 (t of d, J_{PC} = 5.8 Hz, J_{CH} = 166.5 Hz), 24.7 (q of d, J_{PC} = 12.0 Hz, J_{CH} = 125.8 Hz), 24.3 (q of d, J_{PC} = 12.1 Hz, J_{CH} = 125.8 Hz), 9.2 (q, J_{CH} = 128.8) ppm. $^{31}P\{^1H\}$ NMR (THF-d_8): δ 61.4 ppm. IR (Fluorolube): 2979 (m), 2931 (m), 1478 (m), 1387 (m), 1296 (m), 974 (s) cm^{-1}. Anal. Calcd for $C_{20}H_{33}F_3IrO_6PS$: C, 35.13; H, 5.16. Found: C, 35.41; H, 5.30.

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Supporting Information Available: Text giving spectroscopic and analytical data for **1**, **2**, and (η^5-C$_5$Me$_5$)IrCl$_2$P(O^i-Pr)$_3$ and variable-temperature NMR spectra and COSY spectrum for the reaction of **1** with HOTf (10 pages). Ordering information is given on any current masthead page.

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