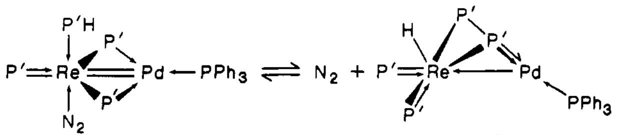
crystals of **5** are heated in vacuo at 60 °C, N_2 is evolved and green microcrystalline $(PCy_2)_2ReH(\mu\text{-}PCy_2)_2Pd(PPh_3)$ (**6**) is obtained.[20] Cooling a pentane solution of **6** at −30 °C under N_2 for several hours gives orange crystals of **5**, thus demonstrating *reversible, N_2-promoted P–H bond activation.* The ^{31}P DNMR spectra of **5**/**6** (Figures 3 and 4, supplementary material) show only **6** above 40 °C and exchange averaging of the inequivalent terminal PCy_2 ligands in **6** with $\Delta G^{\ddagger}_{T_c} = 10.2 \pm 0.2$ kcal/mol (cf. 13.7 ± 0.3 kcal/mol for **3**). Excess PMe_3 reacts with **5** at both metal centers to afford poorly soluble red-orange crystals of $(PCy_2)(PMe_3)_2Re(\mu\text{-}PCy_2)_2Pd(PMe_3)$ (**7**). The molecular structure[21] of **7** (Figure 2E) consists of a planar ReP_2Pd bridge with trigonal-bipyramidal coordination about Re and a Re=Pd double bond (2.7575 (9) Å). Complex **5** is presumably isostructural with **7**, with N_2 trans to PCy_2H on Re, while **6** is proposed to have a donor–acceptor Pd→Re bond and a bent ReP_2Pd bridge, similar to **3**.[22]

$$\underset{\mathbf{4}}{\mathrm{Re(PCy_2)_3(PCy_2H)}} + \tfrac{1}{2}(\mu\text{-}\eta\text{-}\mathrm{C_5H_5})(\mu\text{-}\eta\text{-2-Me-allyl})\mathrm{Pd_2(PPh_3)_2} \rightarrow \tfrac{1}{2}\mathrm{C_5H_5\text{-}C_4H_7} + \underset{\mathbf{5}}{\mathrm{(PCy_2)(PCy_2H)(N_2)Re}(\mu\text{-}\mathrm{PCy_2})_2\mathrm{Pd(PPh_3)}} \qquad (2)$$



5 **6**

P′ = PCy_2

While carbonylation (1 atm, 25 °C) of **5** occurs at Re to give orange crystals of $(PCy_2)(CO)_2Re(\mu\text{-}PCy_2)_2Pd(PPh_3)$ (**8**), reaction of **2b** with CO occurs at both metals to give red-orange crystals of $(PCy_2)(CO)_2Re(\mu\text{-}PCy_2)_2Ir(CO)_2(PCy_2)$ (**9**) in which a PCy_2 ligand has been transferred to the Ir center. The molecular structure[23] of **9** (Figure 2F) consists of trigonal-bipyramidal Re and Ir centers with a planar ReP_2Ir bridge and a covalent Re–Ir single bond (2.9117 (7) Å). Three different bonding modes for the PCy_2 ligand are observed, with planar and pyramidal terminal PCy_2 ligands on Re (Re–P3 = 2.232 (2) Å) and Ir (Ir–P4 = 2.467 (2) Å), respectively. This carbonylation reaction clearly illustrates how PR_2 bridges can promote cooperative reactivity between different metal centers; the Re center adopts a lower oxidation state and favorable trigonal-bipyramidal geometry while the Ir center is forced to bear a marginally stable, pyramidal terminal PCy_2 ligand.[24] Further examples of cooperative reactivity are observed with H_2 in work to be reported elsewhere.[25]

Acknowledgment. We wish to thank S. A. Hill, T. J. Onley, E. A. Conaway, and W. J. Marshall for skilled technical assistance.

Registry No. 1, 87462-44-0; **2a**, 115207-03-9; **2b**, 115207-04-0; **2c**, 115207-05-1; **2d**, 115207-06-2; **3**, 115207-08-4; **4**, 115207-09-5; **5**, 115207-10-8; **6**, 115207-11-9; **7**, 115207-12-0; **8**, 115207-13-1; **9**, 115207-14-2; $[Ir(1,5\text{-}COD)Cl]_2$, 12112-67-3; $[Rh(1,5\text{-}COD)Cl]_2$, 12092-47-6; $(\mu\text{-}\eta\text{-}C_5H_5)(\mu\text{-}\eta\text{-2-Me-allyl})Pd_2(PPh_3)_2$, 54497-76-6; $(\eta\text{-}C_5H_5)Pd(\eta\text{-2-Me-allyl})$, 33593-95-2; PMe_3, 594-09-2; PPh_3, 603-35-0.

Supplementary Material Available: Two figures of ^{31}P NMR spectra of **5** and **6**, four tables of infrared and ^{1}H and ^{31}P NMR spectral data and complete elemental analyses, summary of data collection and refinement, and tables of atom coordinates, thermal parameters, and bond distances and angles for **2d**, **3**, **7**, and **9** (21 pages); listings of structure factors for **2d**, **3**, **7**, and **9** (61 pages). Ordering information is given on any current masthead page.

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[19] A solution of 326 mg (1.24 mmol) of PPh_3 in 20 mL of THF was added to 283 mg (1.25 mmol) of $(\eta\text{-}C_5H_5)Pd(\eta\text{-2-Me-allyl})$ in 20 mL of THF, giving an orange solution to which a solution of 1.20 g (1.23 mmol) of $Re(PCy_2)_3(PCy_2H)$ in 45 mL of THF was added dropwise. After 20 h, the solvent was removed in vacuo, the residue was extracted with 10 mL of pentane, 1 mL of DME was added, and the mixture was cooled at −20 °C for 20 h. The resulting orange crystals were filtered off and dried in vacuo, yielding 610 mg of **5**. Further crops brought the total yield to 1.17 g (69%).

[20] The **5** → **6** conversion is conveniently monitored by infrared spectroscopy as the absorptions due to ν_{PH} (2261 cm^{-1}) and ν_{NN} (2046 cm^{-1}) are replaced by that due to ν_{ReH} (1918 cm^{-1}).

[21] Bond distances and angles; Re–P(1) = 2.384 (2) Å, Re–P(2) = 2.387 (2) Å, Re–P(3) = 2.262 (2) Å, Re–P(4) = 2.378 (2) Å, Re–P(5) = 2.399 (2) Å, Pd–P(1) = 2.328 (2) Å, Pd–P(2) = 2.321 (2) Å, Pd–P(6) = 2.264 (2) Å; $Pd–P–Re_{av}$ = 71.65 (5)°, P(1)–Pd–P(2) = 110.23 (6)°, P(1)–Re–P(2) = 106.12 (6)°, P(4)–Re–P(5) = 178.3 (2)°.

[22] These proposals are based on ^{31}P NMR data which show three-bond P–P coupling of the terminal Re–PCy_2 ligand to the Pd–PPh_3 ligand in **5** (26 Hz) and **8** (15 Hz), while **6** shows no such coupling.

[23] Bond distances and angles: $Ir–C_{av}$ = 1.894 (7) Å, $Re–C_{av}$ = 1.959 (6) Å, Ir–P(1) = 2.369 (2) Å, Ir–P(2) = 2.361 (1) Å, Re–P(1) = 2.370 (1) Å, Re–P(2) = 2.361 (2) Å; $Ir–P–Re_{av}$ = 75.98 (5)°, C(4)–Ir–C(3) = 161.9 (3)°, C(1)–Re–C(2) = 179.4 (3)°, C(81)–P(4)–C(71) = 101.2 (3)°, C(61)–P(3)–C(51) = 105.2 (3)°.

[24] Ir–P(4) is the longest such distance reported; Ir–P distances for μ-PCy_2 range from 2.24 to 2.37 Å; Baker, R. T.; Calabrese, J. C., unpublished results.

[25] Baker, R. T.; Calabrese, J. C.; Glassman, T. E.; Ovenall, D. E. *Organometallics*, manuscript in preparation.

Carbon–Carbon Bond Formation Reactions of the Iodomethane Complex $[Cp(dppe)Ru(ICH_3)]PF_6$

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Summary: The new iodomethane complex $[Cp(dppe)Ru(IMe)](CF_3SO_3)$ (**1a**) is formed by a new synthetic route, the reaction between methyl trifluoromethanesulfonate and Cp(dppe)RuI (dppe = 1,2-bis(diphenylphosphino)ethane). The hexafluorophosphate salt **1b** reacts with a wide range of nucleophiles, including enamines and lithium enolates, affording C-methylation products. In the first reported case of carbon–carbon bond formation via a halocarbon complex, complex **1** regioselectively methylates 1-(*N*-pyrrolidino)cyclohexene producing 2-methylcyclohexanone in good yield, after hydrolysis. We also report the synthesis of a new haloarene complex and its equilibration with free iodomethane.

Since our initial crystallographic demonstration of transition-metal–halocarbon coordination in 1982,[1] several further examples have been reported. Simple haloalkanes, haloarenes,[2a–k] and even chelated fluoroarenes[3a,b] have been

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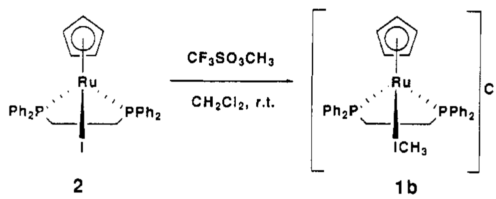
[1] Crabtree, R. H.; Faller, J. W.; Mellea, M. F.; Quirk, J. M. *Organometallics* 1982, *1*, 1361.

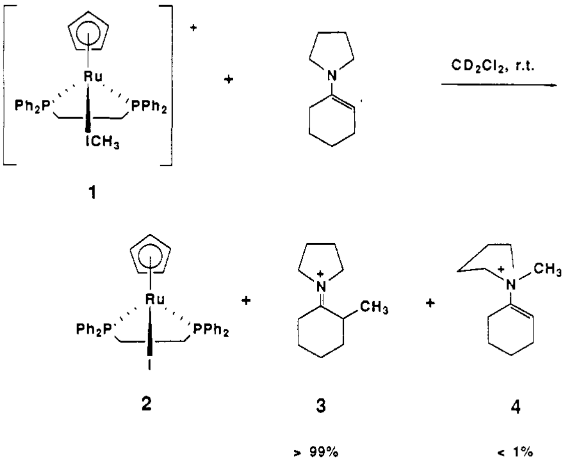
shown to bind to transition-metal ions via the halogen lone pair. We recently reported[2g] that $[IrH_2(PPh_3)_2(IMe)_2]PF_6$ methylates hindered amines ca. 10^6 times faster than does free iodomethane. This suggested that iodomethane complexes might be useful as selective methylating reagents in organic synthesis. A recent report by Gladysz and coworkers[2i] describes the synthesis of a series of alkyl halide complexes of the formula $[CpRe(NO)(PPh_3)(XR)]^+$, which alkylate tertiary phosphines, yielding phosphonium salts. We now wish to report the novel synthesis, characterization, and methylation reactions of a new iodomethane complex, $[Cp(dppe)Ru(ICH_3)]X$ (**1a**, X = $CF_3SO_3^-$; **1b**, X = PF_6^-; dppe = 1,2-bis(diphenylphosphino)ethane).

Up to now, halocarbon complexes have been prepared from the halocarbon itself. We now find that treatment of Cp(dppe)RuI (**2**)[4a] with 1 equiv of methyl trifluoromethanesulfonate in dichloromethane forms the new iodomethane complex **1a** in 85% yield (eq 1).[5a] This result may be significant for catalytic applications of these species because, at least in principle, it allows the iodomethane complex to be regenerated from the iodo complex. An alternate synthesis[5b] involves the more conventional Ag(I) abstraction of chloride from Cp(dppe)RuCl in dichloromethane in the presence of excess (ca. 50 equiv) iodomethane, producing complex **1b**, $[Cp(dppe)Ru(ICH_3)]PF_6$, in similar yields. Complex **1b** has been fully characterized[5c] by ^1H, ^{13}C, and ^{31}P NMR. Notably, the ^1H and ^{13}C resonances of the iodomethane are shifted by −0.99 and +11.7 ppm, respectively, upon coordination. In contrast to the broad resonances observed for the iridium bis(iodomethane) complex,[2f] **1** displays a sharp methyl resonance in the ^1H NMR, suggesting slow exchange with free iodomethane on the NMR time scale. The formulation of **1** as an iodomethane complex, rather than a methylruthenium(IV) product of oxidative addition, is evidenced by the lack of coupling of the methyl protons to ^{31}P. In other cyclopentadienylbis(tertiary phosphine)ruthenium methyl complexes, phosphorus coupling of 5–7 Hz is commonly observed.[6a,b]



(1)

In view of the importance of carbon–carbon bond formation in organic synthesis, we initially investigated the reactivity of **1** toward carbon nucleophiles, for example, enamines. As we expected, iodomethane complex **1** is a powerful methylating agent toward such species. Reaction of complex **1b** with 1-(*N*-pyrrolidino)cyclohexene (eq 2) results in complete and essentially instantaneous disappearance of **1** to yield Cp(dppe)RuI (**2**) and the desired iminium salt **3**, identified by ^1H NMR.[7] Integration of the cyclopentadienyl resonance of ruthenium iodide **2** vs the methyl resonances of **3** and **4** shows that the carbon-methylation products are formed in ca. 92% yield with respect to **2**, with a **3**:**4** ratio of >100:1. This result demonstrates the increased regioselectivity of metal-mediated methylation compared to a similar reaction with free iodomethane, in which N-alkylation, a common parasitic reaction in enamine chemistry,[8a] accounts for essentially 100% of the products.[8b,c] The C-alkylation of eq 2 also occurs rapidly at −78 °C with a $t_{1/2}$ of ca. 10 min, consistent with the increased electrophilicity of the methyl carbon upon coordination to cationic ruthenium(II). On a preparative scale,[9] 2-methylcyclohexanone (identified by GC)



(2)

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(2) (a) Burk, M. J.; Crabtree, R. H.; Holt, E. M. *Organometallics* **1984**, *3*, 638. (b) Crabtree, R. H.; Mellea, M. F.; Quirk, J. M. *J. Am. Chem. Soc.* **1984**, *106*, 2913. (c) Barcelo, F.; Lahuerta, P.; Ubeda, M. A.; Foces-Foces, C.; Cano, F. H.; Martinez-Ripoll, M. *J. Chem. Soc., Chem. Commun.* **1985**, 43. (d) Solans, X.; Font-Albana, M.; Aguilo, M.; Miravitlles, C.; Besteiro, J. C.; Lahuerta, P. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1985**, *C41*, 841. (e) Cotton, F. A.; Lahuerta, P.; Sanau, M.; Schwotzer, W.; Solana, I. *Inorg. Chem.* **1986**, *25*, 3526. (f) Barcelo, F.; Cotton, F. A.; Lahuerta, P.; Llusar, R.; Sanau, M.; Schwotzer, W.; Ubeda, M. A. *Organometallics* **1986**, *5*, 808. (g) Burk, M. J.; Segmuller, B.; Crabtree, R. H. *Organometallics* **1987**, *6*, 2241. (h) Barcelo, F.; Cotton, F. A.; Lahuerta, P.; Sanau, M.; Schwotzer, W.; Ubeda, M. A. *Organometallics* **1987**, *6*, 1105. (i) Winter, C. H.; Arif, A.; Gladysz, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 7560. (j) Barcelo, F.; Lahuerta, P.; Ubeda, M. A.; Foces-Foces, C.; Cano, F. H.; Martinez-Ripoll, M. *Organometallics* **1988**, *7*, 584. (k) Liotta, F. J. Jr.; Van Duyne, G.; Carpenter, B. K. *Organometallics* **1987**, *6*, 1010.

(3) (a) Kulawiec, R. J.; Holt, E. M.; Lavin, M.; Crabtree, R. H. *Inorg. Chem.* **1987**, *26*, 2559. (b) Catala, R. M.; Cruz-Garritz, D.; Hills, A.; Hughes, D. L.; Richards, R. L.; Sosa, P.; Torrens, H. *J. Chem. Soc., Chem. Commun.* **1987**, *261*.

(4) (a) Prepared via halide metathesis between Cp(dppe)RuCl[4b] and NaI in methanol. (b) Ashby, G. A.; Bruce, M. I.; Tomkins, I. B.; Wallis, R. C. *Aust. J. Chem.* **1979**, *32*, 1003.

(5) (a) Experimental procedure for **1a**: to a solution of Cp(dppe)RuI[4a] (51.5 mg, 0.074 mmol) in CH_2Cl_2 (10 mL) was added $CH_3OSO_2CF_3$ (9.6 μL, 0.085 mmol, 1.2 equiv; Aldrich Chemical Co.). The resulting solution was stirred under N_2 in the dark overnight and reduced in volume to <5 mL. The product was precipitated as a yellow powder with ether (20 mL) and hexanes (60 mL), collected on a medium-porosity fritted disk, washed with excess hexanes, and dried in vacuo; yield 53.0 mg (82%). (b) Experimental procedure for **1b**: to a suspension of Cp(dppe)RuCl[4b] (400 mg, 0.667 mmol) in CH_2Cl_2 (40 mL) under N_2 was added $AgPF_6$ (177 mg, 0.700 mmol, Aldrich Chemical Co.). The suspension was stirred at room temperature in the dark for 1 h, filtered through Celite, and reduced in volume in vacuo to 5 mL and the product precipitated by addition of ether (30 mL) and pentane (30 mL). The yellow microcrystalline product was collected on a medium porosity fritted disk, washed with excess ether, and dried in vacuo; yield 495 mg (87%). The product is moderately air-sensitive in the solid and more so in solution; it can be kept for over a month if stored under N_2 at −20 °C in the dark. (c) ^1H NMR (250 MHz, CD_2Cl_2): δ 7.70–7.25 (c, P*Ph*, 20 H), 4.96 (s, 5 H, C_5H_5), 3.45, 3.76 (c, CH_2CH_2, 4 H), 1.18 (s, 3 H, CH_3). $^{13}C\{^1H\}$ NMR (62.89 MHz, CD_2Cl_2): δ 132.4–129.4 (aryl), 81.60 (C_5H_5), 27.60 (CH_2), −11.97 (CH_3I). $^{31}P\{^1H\}$ NMR (202.5 MHz, CD_2Cl_2, vs 85% H_3PO_4): δ 75.38 (s). Elemental Anal. (Desert Microanalytics, Tucson, AZ). Calcd for $C_{32}H_{32}F_6IP_3Ru\cdot{}^1/_3CH_3I$: C, 43.21; H, 3.78. Found: C, 43.36; H, 3.77.

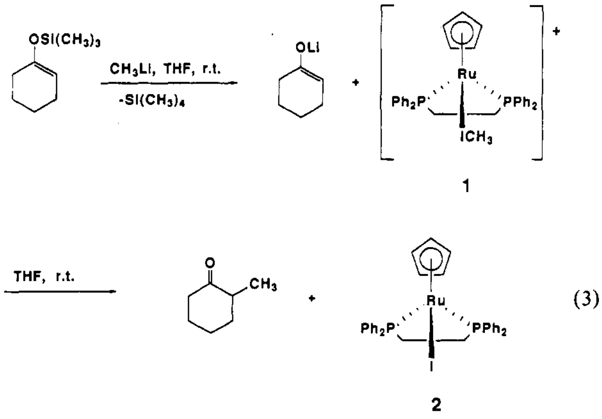
(6) (a) For example, $Cp(PPh_3)_2RuCH_3$: δ 0.29 (t, $^3J_{PH}$ = 5.6 Hz). Blackmore, T.; Bruce, M. I.; Stone, F. G. A. *J. Chem. Soc. A* **1971**, 2376. (b) $[Cp(PPh_3)_2Ru(CH_3)(H)]BF_4$: δ 0.35 (t, $^3J_{PH}$ = 6.3 Hz, CH_3), −7.3 (t, $^2J_{PH}$ = 24 Hz, H). Heinekey, D. M.; Chinn, M. S., private communication, 1988.

(7) ^1H NMR (250 MHz, CD_2Cl_2): δ 1.338 (d, $^3J_{HH}$ = 7.30 Hz).

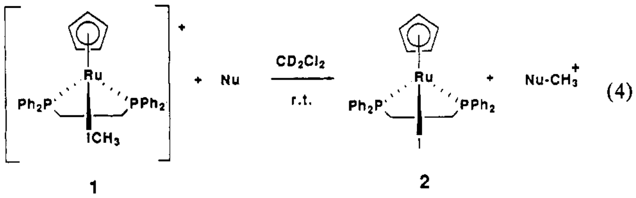
(8) (a) Curphey, T. J.; Hung, J. C.; Chu, C. C. C. *J. Org. Chem.* **1975**, *40*, 607. (b) In an NMR experiment, the enamine reacts with iodomethane (1 equiv, CD_2Cl_2, room temperature, 2.5 h) to produce the *N*-methylammonium salt **4** (δ 3.389 (s)), with only a trace of 2-methyliminium salt **3**[7] (≪1%) observable.[8c] (c) Kulawiec, R. J., unpublished results, 1988.

is isolated in >80% yield, after aqueous workup. This reaction demonstrates the first application of a transition-metal halocarbon complex in a selective carbon–carbon bond formation reaction.

Other carbon nucleophiles are also methylated by 1. The lithium enolate, shown in eq 3 and obtained via desilylation of the corresponding trimethylsilyl enol ether, reacts with **1b** in THF to yield 2-methylcyclohexanone (60%, by GC[10]) as shown in eq 3. The silyl enol ether itself, however, is not sufficiently nucleophilic to react with 1.

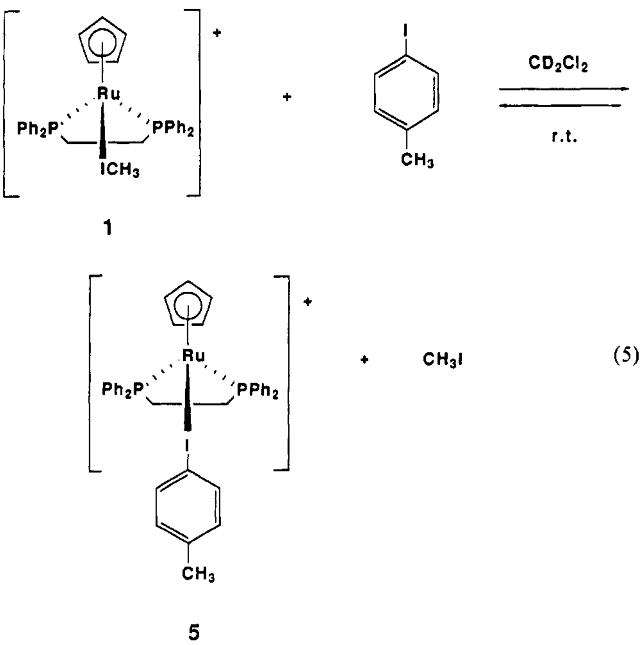


In addition to carbon nucleophiles, the iodomethane complex 1 also reacts with a wide range of other nucleophiles (eq 4). In all cases, addition of the nucleophile to the iodomethane complex **1b** results in rapid and quantitative formation of the ruthenium iodide complex **2** and the corresponding methylation products, as identified by ^{1}H NMR. Similar reactions with hindered amines[2g] and phosphines[2i] are known for other iodomethane complexes. In striking contrast, the iridium complex $[IrH_2(PPh_3)_2(IMe)_2]SbF_6$[2g] gives ligand displacement, rather than methylation, with these nucleophiles. Reaction of **1b** with less nucleophilic species such as acetone, acetonitrile, and pyridine resulted in complete displacement to generate free iodomethane and the cationic complexes $[Cp(dppe)Ru(L)]PF_6$ (L = $(CH_3)_2CO$, CH_3CN, C_5H_5N), the identities of which were verified by independent synthesis.[11]



Nu = Cl⁻, PhCO₂⁻, NEt₃, PMe₃

A new iodoarene complex, $[Cp(dppe)Ru(IC_6H_4\text{-}p\text{-}CH_3)]PF_6$ (**5**), can also be prepared by a procedure similar to that employed for **1b** and is characterized by ^{1}H NMR.[12] Iodomethane and *p*-iodotoluene compete for the coordination site at ruthenium as depicted in eq 5. The equilibrium constant for eq 4 is 0.17 ± 0.02 (298 K), determined by ^{1}H NMR. The value of *K* apparently reflects both the increased steric demands and lower basicity of the *p*-iodotoluene ligand. Further experiments to quantify the relative and absolute M–XR bond strengths in ruthenium(II) halocarbon complexes are in progress.



In conclusion, we have shown a new synthetic route to a transition-metal iodomethane complex, which we expect to be general for the reaction of carbon electrophiles with other coordinatively saturated, oxidation-resistant halide complexes.

Furthermore, we have demonstrated the first example of selective carbon–carbon bond formation by a transition-metal halocarbon complex. We suspect that this reaction may have implications for methylation in organic synthesis and are currently investigating its scope and limitations.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work and Martin McGrath for obtaining the ^{31}P NMR spectrum.

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(9) In a typical procedure, to a cooled (0 °C) solution of **1b** (100 mg, 0.117 mmol) in CH_2Cl_2 (15 mL) was added the enamine (0.37 mL, 2.35 mmol, 20 equiv). After being warmed to room temperature (1 h), the reaction mixture was hydrolyzed with acetate buffer (15 mL, 0.2 M, pH 4) for 1 h, the organic layer separated, washed with dilute HCl, $NaHCO_3$, and brine, dried over Na_2SO_4, filtered, and evaporated. The residue was dissolved in hexanes, filtered through a short column of silica to remove the ruthenium complex, and analyzed by GC.

(10) The aqueous workup employed precluded quantification of any O-methylation products which may have been formed.

(11) Davies, S. G.; Scott, F. *J. Organomet. Chem.* **1980**, *188*, C41.

(12) ^{1}H NMR (250 MHz, CD_2Cl_2): δ 7.75–7.20 (c, P*Ph*), 6.649 (d, $^3J_{HH}$ = 8.1 Hz, *Ar*I), 6.500 (d, $^3J_{HH}$ = 8.1 Hz, *Ar*I), 4.902 (s, C_5H_5), 2.75–2.20 (c, CH_2CH_2), 2.243 (s, Ar*Me*). We have not yet been able to prepare analytically pure samples of **5**; the major contaminants appear to be **2** and *p*-iodotoluene, by ^{1}H NMR.

Synthesis and Structure of 2,3-Bis(trimethylsilyl)-5-(trichlorogermyl)-2,3-dicarba-1-germa-*closo*-heptaborane(6): A Novel, Potential Intermediate for Extended Germacarboranes of Mixed Valences

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Received May 20, 1988

Summary: The reaction of *closo*-1-Sn-2,3-$(Me_3Si)_2$-2,3-$C_2B_4H_4$ (I) with a slight excess of $GeCl_4$ at 135 °C in the absence of solvent produced a novel germacarborane,

0276-7333/88/2307-1893$01.50/0