Acknowledgment. We are grateful to the National Science Foundation for support of this work to G.H.R. (RII-8520554).

Supplementary Material Available: Tables of crystal data, bond distances and angles, final fractional coordinates, and thermal parameters (6 pages); a listing of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

Unsaturated, PCy_2-Bridged Re–M Heterobimetallics (M = Rh, Ir, Pd; Cy = Cyclohexyl): Metal–Metal Bond Isomerism, Reversible P–H Bond Activation, and Cooperative Reactivity†

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Received May 20, 1988

Summary: The new d^4-d^8 heterobimetallics $(PCy_2)_2Re(\mu\text{-}PCy_2)_2M(1,5\text{-}COD)$ (M = Rh, Ir; COD = cyclooctadiene) are proposed, on the basis of ^{31}P DNMR, to exist in two isomeric forms: one with pseudotetrahedral (PT) coordination about M and an M=Re double bond and the other with square-planar (SP) coordination about M and an M→Re donor–acceptor bond. Structural models for this metal–metal bond isomerism are provided by $(PCy_2)_2Re(\mu\text{-}PCy_2)_2Ir(PMe_3)_2$ (PT, Re–Ir = 2.6573 (5) Å) and $[(PCy_2)_2ReH(\mu\text{-}PCy_2)_2Rh(1,5\text{-}COD)]BF_4$ (SP, Re–Rh = 2.9361 (8) Å). Reversible P–H bond activation is observed for $(PCy_2)(PCy_2H)(N_2)Re(\mu\text{-}PCy_2)_2Pd(PPh_3)$(*Pd=Re*) and $(PCy_2)_2ReH(\mu\text{-}PCy_2)_2Pd(PPh_3)$(*Pd→Re*) and carbonylation of the Ir-COD complex occurs at both metal centers to give $(PCy_2)(CO)_2Re(\mu\text{-}PCy_2)_2Ir(CO)_2(PCy_2)$ in which a PCy_2 ligand has been transferred to Ir.

One approach to the development of new selective transition-metal catalysts involves the use of heterobimetallic complexes in which each metal center performs a different function.[1] In most soluble heterobimetallic complexes one or both metal centers are electronically saturated,[2] and reactivity at both metal centers without fragmentation is rarely observed.[3] We have recently shown that reactions of groups 8–10 transition-metal complexes with early transition-metal-containing phosphines that contain $\mathrm{M}\overset{\leftarrow}{=}\mathrm{P}$ double bonds lead directly to heterobimetallics in which the early metal center is electronically unsaturated.[4] In this report we describe the synthesis and metal–metal bond isomerism of $(PCy_2)_2Re(\mu\text{-}PCy_2)_2M(1,5\text{-}COD)$ (M = Rh, Ir; COD = cyclooctadiene), the synthesis of $(PCy_2)(PCy_2H)(N_2)Re(\mu\text{-}PCy_2)_2Pd(PPh_3)$ and reversible P–H bond activation to give $(PCy_2)_2ReH(\mu\text{-}PCy_2)_2Pd(PPh_3)$, and the cooperative addition of CO to the M = Ir complex to give $(PCy_2)(CO)_2Re(\mu\text{-}PCy_2)_2Ir(CO)_2(PCy_2)$.

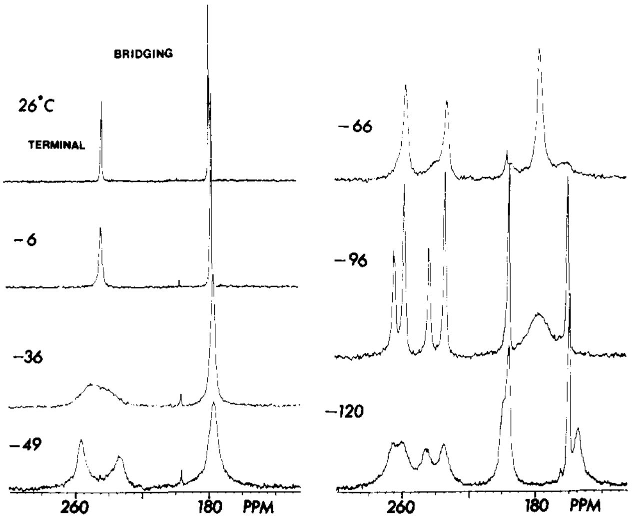

Figure 1. $^{31}P\{^1H\}$ DNMR spectra of $(PCy_2)_2Re(\mu\text{-}PCy_2)_2Ir(1,5\text{-}COD)$ (**2b**) in THF-d_8–pentane (1:2).

Displacement of chloride ion from $[M(1,5\text{-}COD)Cl]_2$[5] by the homoleptic $[Re(PCy_2)_4]^-$ anion[6] (**1**) gives the unsaturated heterobimetallics $(PCy_2)_2Re(\mu\text{-}PCy_2)_2M(1,5\text{-}COD)$ (M = Rh, **2a**; M = Ir, **2b**) as dark purple and black microcrystalline solids in high yield.[7]

$$\underset{\mathbf{1}}{[Li(DME)][Re(PCy_2)_4]} + {}^1/_2[M(1,5\text{-}COD)Cl]_2 \rightarrow \underset{\substack{\mathbf{2a},\ M = Rh\\ \mathbf{2b},\ M = Ir}}{(PCy_2)_2Re(\mu\text{-}PCy_2)_2M(1,5\text{-}COD)} \quad (1)$$

Complexes **2a**,**b** have been characterized by IR and ^1H and ^{31}P NMR spectroscopy and by complete elemental analysis (Tables I–IV, supplementary material). The ^{31}P DNMR spectra of **2b** (Figure 1) indicate the presence of two isomers, each with four inequivalent PCy_2 ligands. Both isomers undergo two different dynamic processes, proposed to be inversion of the bent ReP_2Ir bridge ($\Delta G^{\ddagger}_{T_c} = 9.7 \pm 0.2$ [9.1 ± 0.2] kcal/mol for the major [minor] isomer)[8,9] and rotation

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† Contribution no. 4670.

[1] For applications to heterogeneous catalysis see: Sinfelt, J. H. *Bimetallic Catalysts: Discoveries, Concepts, and Applications*; Wiley: New York, 1983. Sinfelt, J. H. *Acc. Chem. Res.* **1987**, *20*, 134–139.

[2] (a) Roberts, D. A.; Geoffroy, G. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Chapter 40. (b) Bullock, R. M.; Casey, C. P. *Acc. Chem. Res.* **1987**, *20*, 167–173. (c) Bruce, M. I. *J. Organomet. Chem.* **1983**, *242*, 147–204; **1985**, *283*, 339–414.

[3] For PR_2-bridged examples see: (a) Langenbach, H.-J.; Vahrenkamp, H. *Chem. Ber.* **1979**, *112*, 3390–3412. (b) Roberts, D. A.; Steinmetz, G. R.; Breen, M. J.; Shulman, P. M.; Morrison, E. D.; Duttera, M. R.; DeBrosse, C. W.; Whittle, R. R.; Geoffroy, G. L. *Organometallics* **1983**, *2*, 846–855. (c) Finke, R. G.; Gaughan, G.; Pierpont, C.; Noordik, J. H. *Organometallics* **1983**, *2*, 1481–1483. (d) Horton, A. D.; Mays, M. J.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1985**, 247–250. (e) Guesmi, S.; Taylor, N. J.; Dixneuf, P. H.; Carty, A. J. *Organometallics* **1986**, *5*, 1964–1969.

[4] (a) Baker, R. T.; Tulip, T. H.; Wreford, S. S. *Inorg. Chem.* **1985**, *24*, 1379–1383. (b) Baker, R. T.; Tulip, T. H. *Organometallics* **1986**, *5*, 839–845. (c) Baker, R. T.; Fultz, W. C.; Marder, T. B.; Williams, I. D. *Organometallics*, to be submitted for publication.

[5] (a) M = Rh: Giordano, G.; Crabtree, R. H. *Inorg. Synth.* **1979**, *19*, 218. (b) M = Ir: Herde, J. L.; Lambert, J. C.; Senoff, C. V. *Inorg. Synth.* **1974**, *15*, 18.

[6] Baker, R. T.; Krusic, P. J.; Tulip, T. H.; Calabrese, J. C.; Wreford, S. S. *J. Am. Chem. Soc.* **1983**, *105*, 6763–6765.

[7] In a typical preparation, a solution of 366 mg (0.5 mmol) of $[Ir(1,5\text{-}COD)Cl]_2$ in 10 mL of THF was added dropwise to a solution of 1.07 g (1.0 mmol) of **1** in 25 mL of THF, giving a red-brown solution. After 3 h the solvent was removed in vacuo and the residue extracted with 25 mL of hexane and filtered. Removal of the hexane in vacuo yielded 1.05 g of dark solid **2b** (82%). Microcrystalline product was obtained by dissolution in a minimum volume of DME, followed after 1 h by filtration and drying in vacuo.

[8] $\Delta G^{\ddagger}_{T_c}$ was estimated by using the Eyring equation for two-site exchange. Cf. Sandstrom, J. *Dynamic NMR Spectroscopy*; Academic: New York, 1982.

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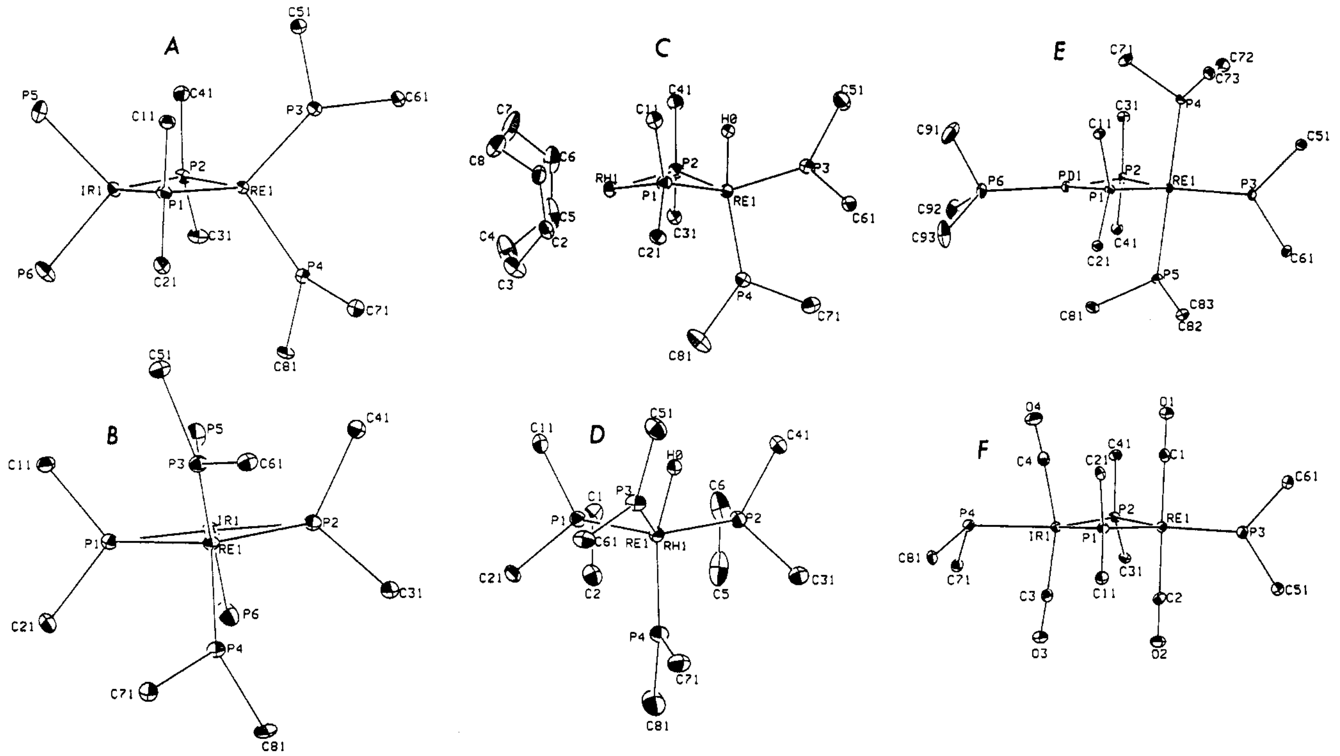
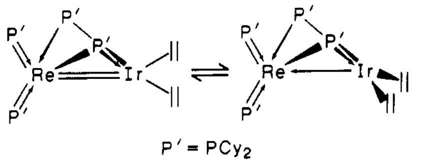


Figure 2. (A) Molecular structure of $(PCy_2)_2Re(\mu\text{-}PCy_2)_2Ir(PMe_3)_2$ (**2d**). Hydrogen and carbon atoms (except C_α of PCy_2) are omitted for clarity. (B) Molecular structure of **2d** viewed down the Re–Ir bond. (C) Molecular structure of $[(PCy_2)_2ReH(\mu\text{-}PCy_2)_2Rh(1,5\text{-}COD)]BF_4$ (**3**). Hydrogen and cyclohexyl carbon atoms (except C_α) are omitted for clarity. (D) Molecular structure of **3** viewed down the Re–Rh bond. (E) Molecular structure of $(PCy_2)(PMe_3)_2Re(\mu\text{-}PCy_2)_2Pd(PMe_3)$ (**7**). Hydrogen and cyclohexyl carbon atoms (except C_α) are omitted for clarity. (F) Molecular structure of $(PCy_2)(CO)_2Re(\mu\text{-}PCy_2)_2Ir(PCy_2)(CO)_2$ (**9**). Hydrogen and cyclohexyl carbon atoms (except C_α) are omitted for clarity.

about the Re-P double bond ($\Delta G^{\ddagger}_{T_c}$ = 8.4 ± 0.2 [6.7 ± 0.3] kcal/mol).[10] Since the $Re(PCy_2)_2$ fragment is isoelectronic with IrL_2, the isomerism presumably stems from both square-planar and tetrahedral coordination about Ir[11] with a donor–acceptor Ir→Re and a covalent Ir=Re double bond, respectively, as shown by EHMO calculations for $[Rh(CO)_2(PH_2)]_2$.[12] A third dynamic process, namely, rotation of the IrL_2 plane with respect to the IrP_2 bridge plane, then interconverts the two isomers.[13] The Rh analogue **2a** shows similar behavior.



Reaction of **2a,b** with excess PMe_3 affords black crystals of $(PCy_2)_2Re(\mu\text{-}PCy_2)_2M(PMe_3)_2$ (**2c,d**). The ^{31}P DNMR spectra of **2c,d** show only one isomer down to −120 °C and no evidence for the bridge inversion process. The molecular structure[14] of **2d** (Figure 2A) confirms the presence of a planar ReP_2Ir bridge, pseudotetrahedral coordination about Re and Ir, and a Re=Ir double bond (2.6573 (5) Å). Figure 2B shows that the conformations of the PC_2 planes of the terminal PCy_2 ligands render all four PCy_2 ligands inequivalent. Protonation of **2a** with $HBF_4{\cdot}Et_2O$ in THF occurs at Re, yielding dark green crystals of $[(PCy_2)_2ReH(\mu\text{-}PCy_2)_2Rh(1,5\text{-}COD)]BF_4$ (**3**). The molecular structure[15] of this d^2–d^8 heterobimetallic (Figure 2C,D) consists of a bent[16] ReP_2Rh bridge, with square-planar coordination about Rh, square-pyramidal coordination about Re,[17] and a donor–acceptor Rh→Re bond (2.9361 (8) Å).

The reaction of pseudotetrahedral $Re(PCy_2)_3(PCy_2H)$ (**4**) (obtained by protonation of **1** with 1 equiv of H_2O in THF) with $(\mu\text{-}\eta\text{-}C_5H_5)(\mu\text{-}\eta\text{-}2\text{-Me-allyl})Pd_2(PPh_3)_2$[18] in THF under a nitrogen atmosphere gives orange crystals of $(PCy_2)(PCy_2H)(N_2)Re(\mu\text{-}PCy_2)_2Pd(PPh_3)$ (**5**).[19] When

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(9) Similar barriers to MP_2M ring inversion have been observed for $[Cp_2M(\mu\text{-}PEt_2)]_2$ (M = Ti, Zr, Hf). Baker, R. T.; Geiger, W. E.; Van Order, N., manuscript in preparation.

(10) $M{=}PR_2$ rotational barriers range from 5.8 kcal/mol in $(\eta\text{-}C_5Me_5)Ti(PCy_2)_2(PMe_3)$ (estimated from DESR spectra; Baker, R. T.; Calabrese, J. C.; Krusic, P. J.; Ortiz, J. V. *Organometallics*, manuscript in preparation) to 10.3 kcal/mol in $(\eta\text{-}C_5H_5)W(CO)_2[P(t\text{-}Bu)_2]$; Jorg, K.; Malisch, W.; Reich, W.; Meyer, A.; Schubert, U. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 92–93.

(11) Conversion of the tetrahedral-planar isomer to the tetrahedral–tetrahedral isomer occurs rapidly (>600 s^{-1}) upon 1e reduction of $\{Rh(CO)_2[\mu\text{-}P(t\text{-}Bu)_2]\}_2$. Cf. Gaudiello, J. G.; Wright, T. C.; Jones, R. A.; Bard, A. J. *J. Am. Chem. Soc.* **1985**, *107*, 888–897.

(12) Kang, S.-K.; Albright, T. A.; Wright, T. C.; Jones, R. A. *Organometallics* **1985**, *4*, 666–675.

(13) Broadening of the terminal PCy_2 ligand resonances below −100 °C is attributed to hindered rotation about the P–C bonds, giving an ensemble of chemical shifts for each resonance.

(14) Bond distances and angles: Re–P(1) = Re–P(2) = 2.359 (2) Å, Re–P(3) = 2.234 (2) Å, Re–P(4) = 2.209 (2) Å, Ir–P(1) = 2.269 (2) Å, Ir–P(2) = 2.263 Å, Ir–P(5) = 2.242 (2) Å, Ir–P(6) = 2.252 (2) Å; Ir–P-Re_{av} = 70.11 (5)°, P(1)–Ir–P(2) = 113.05 (7)° P(5)–Ir–P(6) = 95.8 (1)°, P(1)–Re–P(2) = 106.46 (7)°, P(3)–Re-P(4) = 102.55 (7)°.

(15) Bond distances and angles: Re–P(1) = 2.281 (2) Å, Re–P(2) = 2.323 (2) Å, Re–P(3) = 2.217 (2) Å, Re–P(4) = 2.244 (2) Å, Re–H = 1.53 (6) Å, Rh–P(1) = 2.355 (2) Å, Rh–P(2) = 2.370 (2) Å; Rh–P–Re_{av} = 78.01 (7)°, P(1)–Rh–P(2) = 97.82 (8)°, P(1)–Re–P(2) = 101.32 (8)°, P(1)–Re–P(3) = 111.27 (8)°, P(1)–Re–P(4) = 106.65 (8)°, P(1)–Re–H = 92 (2)°, P(3)–Re–P(4) = 97.78 (8)°.

(16) The dihedral angle between the P(1)–Rh–P(2) and P(1)–Re–P(2) planes is 25.8°.

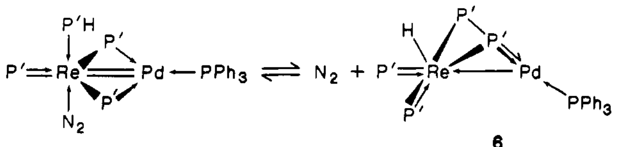
(17) The square base is defined by P(2), P(3), P(4), and H(0), with P(1) as the apex (Figure 2C,D).

(18) Werner, H.; Tune, D.; Parker, G.; Kruger, C.; Brauer, D. J. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 185–186.

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

$$\underset{\mathbf{4}}{Re(PCy_2)_3(PCy_2H)} + {}^1/_2(\mu\text{-}\eta\text{-}C_5H_5)(\mu\text{-}\eta\text{-}2\text{-Me-allyl})Pd_2(PPh_3)_2 \rightarrow {}^1/_2C_5H_5\text{–}C_4H_7 + \underset{\mathbf{5}}{(PCy_2)(PCy_2H)(N_2)Re(\mu\text{-}PCy_2)_2Pd(PPh_3)} \quad (2)$$

°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]



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; $(\mu\text{-}\eta\text{-}C_5H_5)(\mu\text{-}\eta\text{-}2\text{-Me-allyl})Pd_2(PPh_3)_2$, 54497-76-6; $(\eta\text{-}C_5H_5)Pd(\eta\text{-}2\text{-Me-allyl})$, 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 ^1H 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 $(\eta\text{-}C_5H_5)Pd(\eta\text{-}2\text{-Me-allyl})$ 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; $Pd\text{–}P\text{–}Re_{av}$ = 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: $Ir\text{–}C_{av}$ = 1.894 (7) Å, $Re\text{–}C_{av}$ = 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; $Ir\text{–}P\text{–}Re_{av}$ = 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.