mixture of **5c** (332 mg, 1 mmol) and **18** (167 mg, 1 mmol) in hexane (7 mL), and the reaction mixture then was worked up. The products were identified as 2,3,3,5-tetramethyl-2,5-diphenyl-5-sila-2,3-digermahexane (**19**, 47%) and 2,4,4-trimethyl-2-phenyl-2-sila-4-germapentane (**20**, 22%).

2,3,3,5-Tetramethyl-2,5-diphenyl-5-sila-2,3-digermahexane (19). To a solution of **5c** (368 mg, 1.1 mmol) in THF (7 mL) was added at −78 °C a solution of **3b** prepared from 1,1,2,2-tetramethyl-1,2-diphenyldisilane (181 mg, 0.67 mmol) and lithium (23 mg, 3.4 mmol) in THF (3 mL). After 0.5 h of stirring at the same temperature, the reaction was quenched with saturated aqueous NH_4Cl, and the mixture was extracted with ether. The ethereal extract was chromatographed on a silica gel column (hexane) to give **19** (352 mg, 74%): bp 150 °C (0.35 mmHg, Kugelrohr); IR (film) 1425, 1250, 1115, 820, 785, 730, 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.17 (2 H, s, CH_2), 0.20 (6 H, s, Me_2Ge), 0.24 (6 H, s, Me_2Si), 0.44 (6 H, s, Me_2PhGe), 7.28–7.34 (6 H, m, Ph), 7.37–7.40 (2 H, m, Ph), 7.44–7.48 (2 H, m, Ph). Anal. Calcd for $C_{19}H_{30}Ge_2Si$: C, 52.86; H, 7.00. Found: C, 52.78; H, 6.96.

2,4,4-Trimethyl-2-phenyl-2-sila-4-germapentane (20). To a solution of **18** (502 mg, 3 mmol) in THF (7 mL) was added dropwise at −78 °C a solution of **3b**, prepared from 1,1,2,2-tetramethyl-1,2-diphenyldisilane (487 mg, 1.8 mmol) and lithium (62 mg, 9 mmol) in THF (3.5 mL). After 0.5 h of stirring at the same temperature, the reaction was quenched with saturated aqueous NH_4Cl, and the mixture was extracted with ether. The extract was washed with water and saturated aqueous NaCl, dried over anhydrous $MgSO_4$, and concentrated. Distillation of the residue under reduced pressure gave **20** (734 mg, 92%): bp 150 °C (13 mmHg, Kugelrohr); IR (film) 1430, 1250, 1115, 1025, 810, 730, 695, 600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.08 (2 H, s, CH_2), 0.10 (9 H, s, Me_3Ge), 0.28 (6 H, s, Me_2Si), 7.30–7.36 (3 H, m, Ph), 7.49–7.54 (2 H, m, Ph). Anal. Calcd for $C_{12}H_{22}GeSi$: C, 53.99; H, 8.31. Found: C, 54.04; H, 8.39.

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Registry No. 1, 1719-57-9; 2, 6727-64-6; 3a, 18489-76-4; 3b, 3839-31-4; 3c, 25149-72-8; 3d, 17946-71-3; 4a, 119795-94-7; 4b, 21082-16-6; 4c, 119795-95-8; 4d, 119795-96-9; 5a, 119795-97-0; 5b, 119795-98-1; 5c, 119795-99-2; 6a, 119796-00-8; 6b, 79180-86-2; 6c, 119796-01-9; 6d, 119796-02-0; 7a, 21458-78-6; 7b, 119796-03-1; 7c, 119796-04-2; 8, 119796-05-3; 9, 119796-06-4; 10, 119796-07-5; 13, 119796-08-6; 14, 2344-80-1; 15, 18027-71-9; 16, 1833-51-8; 17, 1027-86-7; 18, 5830-55-7; 19, 119796-09-7; 20, 119796-10-0; chlorotrimethylgermane, 1529-47-1; chlorodimethylphenylsilane, 768-33-2; 1,1,2,2-tetramethyl-1,2-diphenyldisilane, 1145-98-8; 1,1,2,2-tetramethyl-1,2-diphenyldigermane, 22702-72-3; chlorotrimethyltin, 1066-45-1; 1,3-bis(chloromethyl)-1,1,3,3-tetramethyldisiloxane, 2362-10-9.

Stereoselective Intramolecular C–H Bond Activation in a Dinuclear Iridium Complex

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Reaction of $[(\eta\text{-}C_5Me_5)Ir(CO)]_2$ (1) with diazomethane affords the methylene bridged dimer $[(\eta\text{-}C_5Me_5)Ir(CO)]_2(\mu\text{-}CH_2)$ (2). Compound **2** is formed without fragmentation of the metal–metal double bond in the starting material, as shown by isotopic double-labeling experiments. Compound **2** crystallizes in the monoclinic space group $C2/c$ (No. 15) with a = 11.367 (4) Å, b = 13.994 (3) Å, c = 14.458 (2) Å, β = 97.85°, V = 2271.8 Å^3, and Z = 8. The Ir–Ir distance is 2.689 Å. Protonation of **2** with $HBF_4{\cdot}Et_2O$ affords a cationic species, **3**. Analytical and spectroscopic data are consistent with the formulation $\{[(\eta\text{-}C_5Me_5Ir(CO)]_2(\mu\text{-}CH_2)(\mu\text{-}H)\}BF_4$. Monitoring of the protonation reaction by ^1H NMR at low temperatures indicates that the inital protonation is stereoselective to give predominantly the cis isomer of **3** as the kinetic product. A slow isomerization occurs to give ultimately the trans isomer of **3**. Facile site exchange in **3-cis** between the methylene hydrogens and the bridging hydride was detected both by spin saturation transfer and line broadening ($\Delta G^{\ddagger}_{223K}$ = 13 kcal/mol). No such exchange process was detectable in **3-trans**.

Introduction

There is great interest in agostic interactions between transition metals and carbon–hydrogen bonds.[1] An important class of compounds containing such interactions are metal dimers and trimers containing bridging methyl groups. Since the seminal work by Shapley and co-workers[2] which established that $Os_3(CO)_{10}(CH_2)H_2$ is in reversible equilibrium with a methyl tautomer, there has been considerable interest in such equilibria, which may serve as models for the activation of C–H bonds in heterogeneous catalytic processes.[3] One synthetic method that has been widely employed in preparation of bridging methyl species is the addition of protic acids to neutral

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methylene-bridged species. Such protonation reactions can lead to at least two quite different outcomes. For example, Casey and co-workers have reported that protonation of $[(\eta\text{-}C_5H_5)Fe(CO)]_2(\mu\text{-}CO)(\mu\text{-}CH_2)$ affords a cationic species with a bridging agostic methyl group.[4] In contrast, Hermann et al. obtained a methylene hydride cation upon protonation of $[(\eta\text{-}C_5H_5)Rh(CO)]_2(\mu\text{-}CH_2)$.[5] A recent theoretical study by Bursten and Cayton points out that the course of these protonation reactions can be predicted by the electronic structure of the parent dimers, provided that a careful distinction is made between the kinetically favored products and the most thermodynamically stable products, which need not be the same.[6a]

In the case of $[(\eta\text{-}C_5H_5)Rh(CO)]_2(\mu\text{-}CH_2)$, Hermann and co-workers reported that protonation with D^+ led to rapid incorporation of deuterium into the methylene sites. These and other observations were interpreted in terms of a rapid equilibrium between the methylene hydride and a bridging methyl tautomer, which was not directly observable. Unfortunately, the instability of the cationic rhodium dimers toward fragmentation prevented a complete study of this process.[5]

In seeking a more tractable system for a detailed study, we have prepared iridium analogues of the previously reported rhodium complexes. The lack of fragmentation has been confirmed by double labeling experiments. We have found that these dimeric iridium complexes allow a detailed study of subtle stereochemical preferences in the oxidative addition and reductive elimination of C–H bonds.

Experimental Section

General Procedures. All manipulations were performed by using standard Schlenk techniques under N_2. All solvents were distilled under N_2. Pentane and ether were distilled from Na/K benzophenone ketyl. THF was distilled from K benzophenone ketyl. Heptane and toluene were distilled from Na benzophenone ketyl. Dichloromethane was distilled from 10% Na/Pb alloy.

Elemental analyses were performed by Galbraith Laboratories. Diazomethane was made by standard procedures using Diazald (Aldrich). Deuterated diazomethane was synthesized by using the standard procedure but with KOD in place of KOH, D_2O in place of H_2O, and carbitol-d_1 in place of carbitol. The acid $H_2C(SO_2CF_3)_2$ was the generous gift of Dr. Allen Siedle of 3M. $D_2C(SO_2CF_3)_2$ was made by exchanging $H_2C(SO_2CF_3)_2$ with D_2O, followed by extraction into ether, and drying over $MgSO_4$. Pure product (90% D) was obtained by sublimation. Isotopically pure ^{191}Ir and ^{193}Ir metal was obtained from Oak Ridge National Laboratories. The metal was converted to $(NH_4)_2IrCl_6$ on a 50-mg scale by standard procedures.[7] Treatment with aqua regia affords H_2IrCl_6[8] which is converted to $[(\eta\text{-}C_5Me_5)IrCl_2]_2$ by refluxing with C_5Me_5H in ethanol.

Spectroscopic Measurements. ^1H NMR spectra were recorded on a Bruker WM-250 MHz spectrometer using the residual solvent protons as an internal reference (CD_2Cl_2, δ 5.32; C_6D_6, δ 7.15). ^{13}C spectra were recorded at 62.89 MHz on the Bruker WM-250. Infrared spectra were obtained on a Nicolet 5DX FTIR. UV spectra were measured on a Cary 219 spectrometer. Electron-impact mass spectra were obtained on a Hewlett-Packard 5985 mass spectrometer. Fast atom bombardment mass spectra (FABMS) were obtained on a Kratos MS80RFA.

Fragmentation Studies for $[(\eta\text{-}C_5Me_5)Ir(CO)]_2$ (1). A toluene solution of $[(\eta\text{-}C_5Me_5)^{191}Ir(CO)]_2$ was diluted until its absorbance at 444 nm equaled 0.470, indicating a 3.69×10^{-5} M concentration ($\epsilon_{444nm} = 1.27 \times 10^4\ M^{-1}\ cm^{-1}$). The procedure was repeated with $[(\eta\text{-}C_5Me_5)Ir^{193}(CO)]_2$ in order to make two stock solutions of equal concentrations. Ten milliliters of each stock solution was combined and concentrated to 5 mL in a Kontes vessel. After the solution was refluxed for 9 days in toluene, the scrambled parent peak (MW = 710) was 35% the size of each isotopically pure parent peak (MW = 708, 712).

Preparation of $[(\eta\text{-}C_5Me_5)Ir(CO)]_2(\mu\text{-}CH_2)$ (2). $[(\eta\text{-}C_5Me_5)Ir(CO)]_2(\mu\text{-}CD_2)$ was made by the same procedure. A black solution of $[(\eta\text{-}C_5Me_5)Ir(CO)]_2$ (1) (0.220 g, 0.31 mmol) in 20 mL of THF at −78 °C was treated dropwise with 20 mL of a 0.3 M diazomethane/ether solution and allowed to sit for 5 min. No color change was observed. When the reaction was complete by IR, the mixture was allowed to warm to room temperature. A fire polished pipet was then used to bubble N_2 through the solution in order to remove any excess diazomethane. After the solution was filtered, the solvent was removed in vacuo. The product was extracted from the residue with 3 × 15 mL of heptane. The heptane was pumped off, and the orange residue was recrystallized from dichloromethane layered with heptane (−25 °C) to yield 0.150 g (0.21 mmol (67%)) of the orange, air-stable product. Anal. Calcd for $C_{23}H_{32}Ir_2O_2$: C, 38.10; H, 4.45. Found: C, 37.90; H, 4.35. IR (CH_2Cl_2): 1920 cm^{-1} (s). ^1H NMR (CD_2Cl_2): δ 2.05 (s, 30 H), 5.09 (s, 2 H). ^1H NMR (C_6D_6): δ 1.97 (s, 30 H), 5.62 (s, 2 H). ^{13}C NMR (C_6D_6): δ 178, 96.4, 58.4 (J_{CH} = 145 Hz), 10.6.

Scrambling Studies for $[(\eta\text{-}C_5Me_5)Ir(CO)]_2(\mu\text{-}CH_2)$ (2). Ten milliliter aliquots of the $[(\eta\text{-}C_5Me_5)^{191}Ir(CO)]_2$ (1-191) and the $[(\eta\text{-}C_5Me_5)^{193}Ir(CO)]_2$ (1-193) stock solutions were combined and concentrated to about 3 mL. The solution was cooled to 195 K, and an excess of diazomethane was added. The solution was allowed to warm to room temperature and then filtered. The solvent was removed in vacuo to leave an orange residue. No crossover peak (MW = 724) was observed by FABMS. Only isotopically pure parent peaks were observed (MW = 722, 726).

Preparation of *trans*-$[(\eta\text{-}C_5Me_5)Ir(CO)]_2(\mu\text{-}CH_2)(\mu\text{-}H)CH(SO_2CF_3)_2$ (3-t). The acid, $H_2C(SO_2CF_3)_2$ (6 mg, 0.025 mmol) was added to an orange solution of $[(\eta\text{-}C_5Me_5)Ir(CO)]_2(\mu\text{-}CH_2)$ (2) (15 mg, 0.021 mmol) in 3 mL of dichloromethane cooled to 273 K. The mixture immediately turned pale yellow. It was allowed to stir at room temperature for 30 min. A quantitative yield of yellow crystals was obtained by concentrating the solution and layering it with ether (200 K). Anal. Calcd for $C_{26}H_{34}Ir_2F_6O_6S_2$: C, 31.07; H, 3.41. Found: C, 31.05; H, 3.49. IR (CH_2Cl_2): 1995 cm^{-1} (s). ^1H NMR (CD_2Cl_2, 298 K): δ 2.15 (s, 30 H), 5.82 (s, 2 H), −14.75 (s, 1 H). ^1H NMR (203 K): δ 2.10 (s, 30 H), 5.67 (s, 2 H), −14.72 (1 H). ^{13}C NMR: δ 167.0, 101.9, 59.4 (J_{CH} = 152 Hz), 10.0.

Preparation of cis-$[(\eta\text{-}C_5Me_5)Ir(CO)]_2(\mu\text{-}CH_2)(\mu\text{-}H)BF_4$ (3-c). Twenty milligrams of $[(\eta\text{-}C_5Me_5)Ir(CO)]_2(\mu\text{-}CH_2)$ (2) (0.0027 mmol) was dissolved in 0.5 mL of CH_2Cl_2 in a small reactor with an NMR tube attached as a side arm. The solution was frozen, and an excess (10 μL) of $HBF_4{\cdot}Et_2O$ was added. The mixture was thawed in a 195 K bath and mixed well. The product 3 was never warmed above 195 K during further manipulations. About 10 mL of cold ether was added through a cannula to precipitate the bright yellow product. The solvent was removed by using a cannula, and the precipitate was washed with 2 × 3 mL of ether to remove excess acid. The solid was dried in vacuo. CD_2Cl_2 was vacuum transferred onto the solid. The solution was added to the NMR tube and frozen. The tube was sealed.

2 + $D_2C(SO_2CF_3)_2$ at 150 K. About 0.4 mL of $CFHCl_2$ was condensed into an NMR tube on a Kontes tap which contained 5.8 mg (0.0069 mmol) of $[(\eta\text{-}C_5Me_5)Ir(CO)]_2(\mu\text{-}CH_2)$ (2) and a small stir bar. The solvent was thawed, and the dimer 2 was dissolved. Next the solution was cooled to 142 K in a pentane/liquid N_2 bath. A cold solution of $D_2C(SO_2CF_3)_2$ (2 mg, 0.0082 mmol) in about 0.1 mL of CD_2Cl_2 was slowly syringed onto the freon solution. The reaction mixture was agitated with the stir bar. After the stir bar was removed from the tube, the sample was frozen and sealed. To conduct the NMR experiments, the sample was thawed in a

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Table I. Summary of Crystal Data for Compound 2

formula	$C_{23}H_{32}Ir_2O_2$
mol wt	724.9
crystal dimens, mm	0.37 × 0.25 × 0.25
system	monoclinic
space group	$C/2c$
a, Å	11.367 (4)
b, Å	13.994 (3)
c, Å	14.458 (2)
α, deg	90
β, deg	97.85 (2)
γ, deg	90
V, Å^3	2271.8
Z	8
d_{calcd}, g/cm^3	2.12
μ (Mo Kα), cm^{-1}	116.7
radiatn	graphite-monochromated Mo Kα (λ = 0.71073 Å)
2θ range, deg	0–48
scan range, $\omega/2\theta$	1.0
scan speed, deg/s	variable
data collected	$h,k,\pm l$
total data	1783
unique data ($I > 3\sigma$)	1323
R	.026
R_w	.031

pentane/liquid N_2 bath and lowered into the NMR probe which had been cooled to 150 K.

Preparation of $[(\eta\text{-}C_5Me_5)IrCO]_2(\mu\text{-}CO)$ (4). All manipulations were carried out in the dark. A solution of $[(\eta\text{-}C_5Me_5)Ir(CO)]_2$ (1) (0.150 g, 0.211 mmol) in 30 mL of toluene was degassed by three freeze–pump–thaw cycles. After the last cycle the Schlenk tube was filled with an atmosphere of CO. The solution was stirred for 30 min, until the reaction was complete by IR. The solvent was removed in vacuo. The product was extracted with 2 × 15 mL of pentane plus 1 mL of dichloromethane. The orange product was recrystallized from dichloromethane/heptane (−25 °C) to give 0.077 g of product (0.104 mmol, 49% yield). Anal. Calcd for $C_{23}H_{30}Ir_2O_3$: C, 31.07; H, 3.41. Found: C, 31.05; H, 3.49. IR (CH_2Cl_2): 1933 (s), 1739 cm^{-1} (s). ^{1}H NMR (CD_2Cl_2) δ 2.09 (s, 30 H). ^{1}H NMR (C_6D_6) δ 1.92 (30 H). ^{13}C NMR (CD_2Cl_2): δ 176.0, 97.3, 10.2.

Preparation of $[(\eta\text{-}C_5Me_5)IrCO]_2(\mu\text{-}H)(\mu\text{-}CO)HC(SO_2CF_3)_2$ (5). The dimer $[(\eta\text{-}C_5Me_5)Ir(CO)]_2(\mu\text{-}CO)$ (4) (5 mg, 0.0068 mmol) and the acid $H_2C(SO_2CF_3)_2$ (3 mg, 0.0075 mmol) were added to an NMR tube on a Kontes tap. CD_2Cl_2 was vacuum transferred into the tube which was then sealed. The solvent was thawed in a 195 K bath, and the reactants were dissolved. Only one product (the trans isomer) was observed by NMR at 203 K, and there was no change in the spectrum over a range of temperatures up to 298 K. A quantitative yield of orange crystals was obtained by concentrating the CD_2Cl_2 and layering the solution with heptane (−25 °C). The same product could be obtained by mixing the reactants at room temperature. Anal. Calcd for $C_{26}H_{32}Ir_2F_6O_7S_2$: C, 30.64; H, 3.17. Found: C, 30.99; H, 3.26. IR (CH_2Cl_2): 2013 (s), 1792 cm^{-1} (s). ^{1}H NMR (CD_2Cl_2): δ 2.13 (s, 30 H), −13.26 (s, 1 H).

X-ray Analysis of $[Cp^*Ir(CO)]_2(\mu\text{-}CH_2)$ (2). A summary of crystal data for 2 is reported in Table I. Diffraction measurements were made on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Preliminary indications of the unit cell based on 25 randomly selected reflections revealed monoclinic symmetry with a = 11.367 (4) Å, b = 13.994 (3) Å, and c = 14.458 (2) Å with β = 97.58°. The space group $C2/c$ with Z = 8 requires that the asymmetric unit consists of one half of the molecule of composition $C_{23}H_{32}Ir_2O_2$ with the bridging methylene carbon residing on the 2-fold axis to generate the entire molecule. There were 1783 reflections collected with $2\theta < 48°$, of those reflections 1323 (74%) with $I \geq 3\sigma(I)$ were adjudged observed.

The structure was solved by locating the position of the iridium atom using the Patterson synthesis. Iterations of least-squares refinement and calculation of difference Fourier maps revealed the entire non-hydrogen structure. The full-matrix refinement of the non-hydrogen atoms and inclusion of the hydrogens in their calculated positions have resulted in convergence to an unweighted residual of 0.026 and a weighted residual of 0.031. Fractional coordinates and isotropic temperature parameters are given in Table II. All intermolecular bond distances and bond angles are within normal ranges (Table III).

Table II. Fractional Coordinates (×10^4) and Isotropic Temperature Parameters for 2[a]

atom	x/a	y/b	z/c	B, Å^2
Ir	173	1664	1599	3.4*[b]
O	−2373 (7)	1520 (9)	823 (7)	6.9 (3)*
C	−1382 (10)	1586 (10)	1156 (8)	4.5 (3)*
CB	0	516 (11)	2500	4.5 (4)*
C1	2158 (9)	1707 (9)	1543 (8)	4.2 (3)*
CM1	3141 (12)	1176 (10)	2125 (11)	6.1 (4)*
C2	1802 (10)	2680 (8)	1676 (9)	4.2 (3)*
CM2	2309 (13)	3324 (11)	2441 (12)	6.9 (4)*
C3	975 (11)	2949 (9)	914 (10)	5.8 (4)*
CM3	377 (14)	3885 (12)	756 (13)	9.8 (5)*
C4	827 (11)	2141 (12)	284 (10)	6.2 (4)*
CM4	52 (15)	2131 (18)	−675 (11)	9.9 (7)*
C5	1575 (10)	1359 (10)	672 (10)	5.1 (4)*
CM5	1744 (13)	439 (12)	204 (12)	7.9 (5)*
HB	−871 (76)	52 (71)	2325 (60)	3.1 (21)
H11	3613	1660	2715	5.0
H21	2773	2910	2910	5.0
H31	820	4375	625	5.0
H41	−566	2500	−840	5.0
H51	1113	0	0	5.0
H12	3725	954	1766	5.0
H13	2840	629	2430	5.0
H22	1711	3651	2735	5.0
H23	2828	3802	2243	5.0
H32	2	4071	1279	5.0
H33	−254	3846	220	5.0
H42	−324	1482	−764	5.0
H43	528	2194	−1161	5.0
H52	2299	56	627	5.0
H53	2119	554	−341	5.0

[a] Standard deviations of the least significant figures are given in parentheses. [b] The isotropic equivalent thermal parameter is given for anisotropic atoms (denoted by an asterisk).

Table III. Selected Bond Lengths and Angles for 2

	Bond Lengths (Å)		
Ir–CB	2.093 (12)	Ir–Ir	2.689 (1)
Ir–C	1.797 (11)	Ir–C1	2.267 (10)
Ir–C4	2.236 (15)	C1–C2	1.440 (18)
C1–CM1	1.498 (17)	C–O	1.164 (14)
	Bond Angles (deg)		
Ir–CB–Ir	80.2 (4)	Ir–Ir–CB	49.9 (4)
C–Ir–CB	90.2 (4)	C–Ir–C1	157.2 (4)
Ir–C1–CM1	129.4 (7)	C–Ir–C4	98.1 (5)
CB–Ir–C1	102.8 (3)	CB–Ir–C4	146.0 (3)
C1–Ir–C4	60.9 (5)	Ir–C–O	176.4 (10)

Results and Discussion

Double Labeling Experiments. In contrast to the apparent lability of the metal–metal double bond in $[(\eta\text{-}C_5H_5)Co(CO)]_2$,[9] we have found that $[(\eta\text{-}C_5Me_5)Ir(CO)]_2$ (1) is a very stable dimeric unit.[10] This conclusion is based on thermolysis of equimolar mixtures of metal-labeled species prepared form isotopically pure ^{191}Ir and ^{193}Ir. In refluxing toluene, 1-191 and 1-193 very slowly ($t_{1/2}$ = ca. 2 weeks) approach a 1:2:1 mixture with 1-191/193 predominating (eq 1). This result is encouraging for the use of this iridium dimer system as a platform for the ex-

(9) Bergman and Hersh have reported that a mixture of $[(\eta\text{-}C_5H_5)Co(CO)]_2$ and $[(\eta\text{-}C_5H_4CH_3)Co(CO)]_2$ rapidly equilibrates with $(\eta\text{-}C_5H_4CH_3)(\eta\text{-}C_5H_5)Co_2(CO)_4$ at −20 °C. Hersh, W. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 5846–5859.

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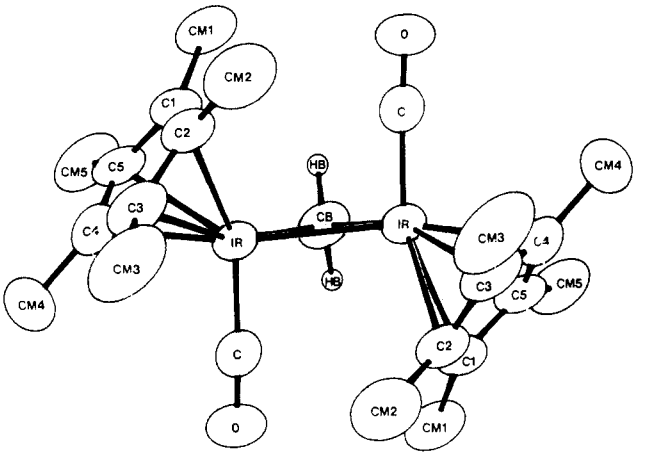

Figure 1. An ORTEP diagram of $[(\eta\text{-}C_5Me_5)Ir(CO)]_2(\mu\text{-}CH_2)$ (**2**) showing 50% probability thermal ellipsoids.

ploration of chemistry occurring at a dinuclear metal center.

$$[Cp^{*191}Ir(CO)]_2 + [Cp^{*193}Ir(CO)]_2 \xrightleftharpoons[\text{toluene}]{\Delta} 2\ Cp^{*191}Ir(\mu\text{-}CO)_2Ir^{193}Cp^{*} \quad (1)$$

Reaction of **1** with diazomethane in THF at 195 K affords $[(\eta\text{-}C_5Me_5)Ir(CO)]_2(\mu\text{-}CH_2)$ (**2**). Spectroscopic data for **2** indicate that the solution structure of **2** is a single isomer (probably trans) with terminal carbonyls. Thus ν(CO) at 1920 cm^{-1} (CH_2Cl_2) and singlet ^1H NMR resonances at δ 2.05 and 5.09 ppm (CD_2Cl_2) are observed. The NMR spectrum is temperature independent down to 203 K. The structure of **2** was confirmed by a single-crystal X-ray diffraction study (vide infra).

The reaction of **1**-191 and **1**-193 with diazomethane was carried out as above. The product **2** was subject to analysis by fast atom bombardment mass spectroscopy (FABMS). No scrambling of the labels was detected (eq 2).

$$\underline{1}\text{-}191 + \underline{1}\text{-}193 \xrightarrow[\text{THF}]{CH_2N_2,\ -78^\circ C} [Cp^{*191}Ir(CO)]_2(\mu\text{-}CH_2) + [Cp^{*193}Ir(CO)]_2(\mu\text{-}CH_2) \quad (2)$$

Solid-State Structure of 2. Consistent with the spectroscopic observations, the structure of **2** consists of an Ir–Ir single bond bridged by a CH_2 group, with the pentamethylcyclopentadienyl ligands disposed in a trans arrangement (Figure 1). The structure is similar to that of $[(\eta\text{-}C_5H_5)Rh(CO)](\mu\text{-}CH_2)$[11] and to that of the mixed Rh/Ir species.[12] The Ir—Ir bond length in **2** is 2.69 Å (Table III) compared to the Ir=Ir distance of 2.55 Å in **1**.[10] A comparable Ir–Ir single bond length of 2.75 Å has been reported for a cyclometalated Ir_2 species.[13]

Protonation of 2. Protonation of **2** in dichloromethane solution ($HBF_4{\cdot}Et_2O$) affords a cationic species that was isolated in good yield by precipitation with diethyl ether. Analytical and spectroscopic data are consistent with the formulation $[(\eta\text{-}C_5Me_5)Ir(CO)]_2(\mu\text{-}CH_2)(\mu\text{-}H)BF_4$ (**3**). Solution ^1H NMR spectroscopy indicates that the product is a mixture of two different species in variable ratios depending upon the temperature at which protonation is carried out. Low-temperature protonation (195 K, CD_2Cl_2) affords predominantly (90%) a product with ^1H NMR

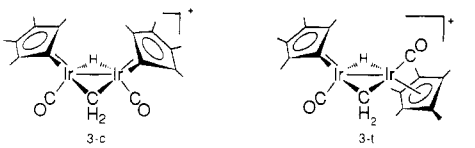

Figure 2. Drawing of the cis and trans forms of the cationic portion of $[(\eta\text{-}C_5Me_5)Ir(CO)]_2(\mu\text{-}CH_2)(\mu\text{-}H)BF_4$ (**3**).

resonances at δ −16.0 (s, 1 H), 2.15 (s, 30 H), 6.42 (d, 1 H), 4.92 ppm (d, 1 H). The spectrum is consistent with predominant formation of the cis isomer **3-c**. As expected of **3-c**, the methylene protons are inequivalent, exhibiting two doublets as expected for an AB spin system ($^2J_{H-H}$ = 2.4 Hz).

Cis to Trans Interconversion in 3. As mentioned above, low-temperature protonation ($HBF_4{\cdot}Et_2O$) of **2** affords predominantly **3-c**. On standing at 298 K, slow isomerization ($t_{1/2}$ = 280 minutes) occurs to give almost entirely **3-t** (Figure 2). The equilibrium ratio **3-t**:**3-c** is about 300:1. From these observations, an approximate $\Delta G^{\ddagger}_{298}$ for the isomerization reaction of 23.4 kcal/mol was calculated. From the equilibrium ratio, it is apparent that **3-t** is more stable than **3-c** by 3.4 kcal/mol. Thus it is clear that the protonation reaction has high selectivity for the kinetic product **3-c** but that the ultimate thermodynamic product is **3-t**.

Methylene/Hydride Site Exchange in 3. Low-temperature reaction of **2** with a DBF_4/HBF_4 mixture showed rapid incorporation of D into the methylene sites of **3-c**, but no D incorporation into the methylene sites of **3-t**. Subsequent **3-c** to **3-t** isomerization leads to incorporation of D into the methylene sites of **3-t**.

3-c exhibits rapid exchange between the bridging hydride and bridging methylene proton environments which was detected by spin saturation transfer (ΔG^{*} = 13.0 kcal/mol, 223 K). The methylene and hydride ^1H NMR resonances begin to broaden at about 240 K. At 298 K the resonances have not yet coalesced; they are broadened into the base line. No such exchange process was detectable in **3-t**.

The methylene/hydride site exchange process in **3-c** likely proceeds through an agostic methyl tautomer formed via a reductive elimination process. No significant isotopic perturbation of resonance (IPR) was observed in partially deuteriated **3**, so direct evidence for such an intermediate was sought by reaction of **1** with methyl cation sources. Thus reaction of **1** with $CH_3O_3SCF_3$ in CD_2Cl_2 at 250 K cleanly affords an 8:1 mixture of **3-c** and **3-t**. This observation is consistent with the intermediacy of a methyl tautomer in the site exchange reaction.

Mechanism of Protonation of 2. The apparent kinetic selectivity for **3-c** in the protonation of **2** prompted us to consider the mechanism of the protonation reaction. Theoretical studies by Bursten and Cayton for the cyclopentadienyl analogue of **2** (with M = cobalt) indicated that the HOMO is a metal–metal bonding orbital that is directed toward the empty bridging position.[6a] The calculations also reveal that the methylene carbon atom carries substantial negative charge. Bursten and Cayton suggest the possibility that two competitive protonation pathways (charge control vs orbital control) may be possible. Assuming that the computational results for $[(\eta\text{-}C_5H_5)Co(CO)]_2(\mu\text{-}CH_2)$ can be qualitatively generalized to the case of **2**, we have attempted to elucidate the mechanism of the protonation reaction.

Protonation of **2** yields various **3-c**:**3-t** ratios depending on the conditions employed. With $HBF_4{\cdot}Et_2O$, protonation at room temperature affords a 40:60 ratio of **3-c**:**3-t**,

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(12) Horlein, R.; Herrmann, W. A.; Barnes, C. E.; Weber, C.; Kruger, C.; Zeigler, M. L.; Zahn, T. *J. Organomet. Chem.* **1987**, 257–272.
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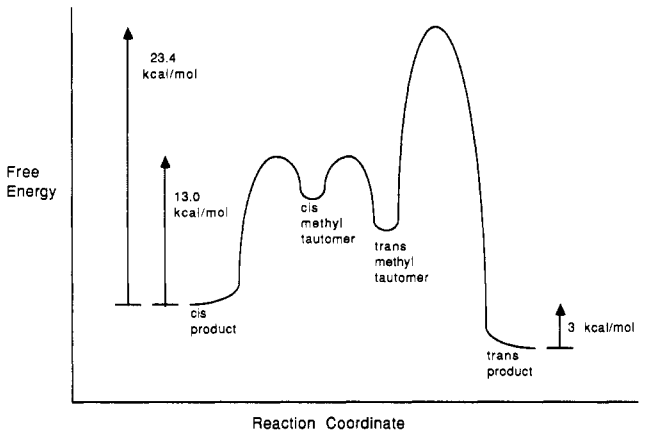

Figure 3. Free energy vs the reaction coordinate for isomerization reaction **3-c** → **3-t**. The energies of the cis and trans methyl tautomers are not precisely known.

whereas protonation at 195 K gives a 90:10 ratio of **3-c**:**3-t**. As expected the higher temperature reaction is less selective, leading to **3-t**, the thermodynamically favored product. When the protonation of **2** was carried out at room temperature with the weaker acid $H_2C(SO_2CF_3)_2$, selectivity for the formation of **3-c** was increaed, but the subsequent isomerization to **3-t** was greatly accelerated.

These observations are consistent with the operation of two competing protonation mechanisms, with the weaker acid allowing for deprotonation/reprotonation to occur. Deprotonation/reprotonation is evidenced by broadening of the $HC(SO_2CF_3)_2$ ^1H NMR resonance.

Protonation of **2** with $D_2C(SO_2CF_3)_2$ (90% D) (195 K, CD_2Cl_2) affords a 9:1 ratio of **3-c**:**3-t**. By ^1H NMR integration, the bridging hydride position in **3-t** was 90% deuterated. In contrast, the bridging hydride site in **3-c** gave a substantial proton signal. Thus formation of **3-t** occurs by orbital-controlled protonation at the metal–metal bond. Formation of **3-c** may occur via charge-controlled protonation at the methylene carbon. The resulting methyl tautomer can then form **3-c** by oxidative addition of either a C–H or C–D bond. The observation of rapid methylene/hydride site exchange in **3-c** noted above indicates that this process is rapid and reversible, so the observed partitioning of D into the methylene and hydride sites represents an equilibrium isotope effect (eq 3).

$$\{[Cp^*Ir(CO)]_2(\mu\text{-}CH_2)(\mu\text{-}D)\}^+ \rightleftharpoons \{[Cp^*Ir(CO)]_2(\mu\text{-}CDH)(\mu\text{-}H)\}^+ \quad (3)$$

If no isotope effect were operative, K_{eq} for eq 3 would be 2. The observed K_{eq} value at 185 K is 6 (±0.5). As expected, deuterium exhibits a preference for the methylene sites. Due to this rapid exchange, clear definition of the kinetic site of protonation requires that D^+ addition be carried out at a temperature where methylene/hydride site exchange is slow.

Protonation of **2** with $D_2C(SO_2CF_3)_2$ at 150 K in $CFHCl_2/CD_2Cl_2$ (4:1) gives a **3-c**:**3-t** ratio of 95:5. Again, the expected statistical ratio of D in the methylene site versus the hydride site in **3-c** would be 2:1. The observed ratio was 8.2 (±1):1 which implies that after protonation at the methylene carbon of **2** to form the intermediate methyl tautomer, oxidative addition of C–H bonds is faster than oxidative addition of C–D bonds. We obtain a value of $k_H/k_D = 4.1$ (±0.5) for the oxidative addition reaction. This is clearly a *kinetic* isotope effect, since the system is not at equilibrium. When the sample temperature was maintained at 150 K for 30 min, there was no change in the methylene/hydride intensity ratios. Brief warming to 230 K establishes the equilibrium of eq 3. At 150 K the K_{eq} is 20 (±10).[14]

Protonation of $[(C_5Me_5)Ir(CO)]_2(\mu\text{-}CO)$. Reaction of **1** with CO affords $[(\eta\text{-}C_5Me_5)Ir(CO)](\mu\text{-}CO)$ (**4**). On the basis of spectroscopic data, **4** likely has the same structure as the rhodium analogue reported by Hermann and coworkers.[15] The ^{13}C NMR spectrum of **4** exhibits only one carbonyl resonance down to 203 K, indicating a facile bridge/terminal exchange process for the carbonyl groups. In contrast to the complex chemistry observed upon protonation of **2**, protonation of **4** with $HBF_4{\cdot}Et_2O$ or $H_2C(SO_2CF_3)_2$ at 298 or at 203 K affords only one product, which was isolated and identified as the $[(\eta\text{-}C_5Me_5)Ir(CO)](\mu\text{-}CO)(\mu\text{-}H)$ cation (**5**). The single terminal CO stretch at 2013 cm^{-1} is consistent with the expected trans structure for **5**, which would arise from orbital-controlled protonation at the metal–metal bond.

Summary and Conclusions

The double-labeling experiment has shown that **1** reacts with diazomethane to give **2** without fragmentation of **1**. Because **1** is isolobal with olefins[16] the reaction can be considered analogous to the cyclopropanation of olefins.

As predicted theoretically,[6] protonation of **2** has been shown to proceed by competing charge- and orbital-controlled mechanisms. Elucidation of the detailed mechanism of the protonation reaction is possible in this system, since the kinetic product **3-c** is only slowly isomerized to the thermodynamic product **3-t**. Our analysis of the isomerization process has allowed the construction of a semiquantitative free energy profile for the isomerization reaction (Figure 3).

The energetic accessibility of the agostic methyl tautomer[17] is firmly established by the observation of methylene/hydride site exchange in **3-c** and by direct synthesis of **3** by methylation of the doubly bonded dimer **1**. Our conclusion that the cis and trans forms of the methyl tautomer are readily equilibrated is based on two key observations: (1) Low-temperature protonation of **2** (which has the trans structure) leads immediately to predominantly **3-c**, presumably via initial formation of the trans methyl tautomer, followed by equilibration to the cis form and oxidative addition to give **3-c**. (2) Primarily **3-c** is formed by direct methylation of **1**. Since synchronous opening of the CO bridges in **1** to give trans structures is clearly favored sterically, interconversion of cis and trans methyl tautomers must be facile. This result is consistent with calculations which indicate that the agostic interaction in the cobalt analogue is relatively weak.[6a]

Thus we are led to conclude that the rate-determining step in **3-c** → **3-t** isomerization is oxidative addition of a C-H bond in the trans methyl tautomer to give **3-t** (Figure 3). It is not clear why the interconversion of **3-c** with the corresponding methyl tautomer is facile in comparison. No calculations are available for cisoid forms of these molecules. It is apparent that in this dinuclear system containing bridging agostic C–H bonds, oxidative addition and reductive elimination rates are extremely sensitive to subtle

(14) Due to the method of detection, larger values of K_{eq} have correspondingly larger relative uncertainties. The directly observable parameter is the ratio of methylene signal intensity to hydride signal intensity. As K_{eq} increases, this ratio asymptotically approaches unity and becomes less sensitive to changes in K_{eq}.

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(17) We favor the formation of an agostic methyl tautomer because this structure gives each iridium an 18-electron count. A methyl tautomer without an agostic C–H interaction is possible but is probably higher in energy.

steric and electronic effects that determine product distribution.[18] We are continuing further investigations of these processes in related systems.

Acknowledgment. We gratefully acknowledge the Petroleum Research Fund and a Cottrell grant from the Research Corp. for financial support. We thank Johnson-Matthey Co. for a loan of iridium salts.

(18) Bergman and co-workers have observed a similar stereoselectivity in methylene/hydride site exchange in a heterodinuclear (Ta/Pt) system.[3a]

Supplementary Material Available: Tables of anisotropic temperature factors and bond lengths and bond angles for **2** (3 pages); a listing of observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

The Facile Transformation of a Hydrido Alkynyl to Vinylidene Ligand on a Tetranuclear Metal Framework, a Process Involving a Reversible Skeletal Rearrangement. Syntheses and Crystal Structures of the Triruthenium–Platinum Clusters $Ru_3Pt(\mu\text{-}H)\{\mu_4\text{-}\eta^2\text{-}C{\equiv}C(t\text{-}Bu)\}(CO)_9(C_8H_{12})$, $Ru_3Pt(\mu\text{-}H)\{\mu_4\text{-}\eta^2\text{-}C{\equiv}C(t\text{-}Bu)\}(CO)_9(Ph_2P(CH_2)_2PPh_2)$, $Ru_3Pt(\mu_4\text{-}\eta^2\text{-}C{=}C(H)t\text{-}Bu)(CO)_9(Ph_2P(CH_2)_2PPh_2)$, and $[Ru_3Pt(\mu\text{-}H)(\mu_4\text{-}\eta^2\text{-}C{=}C(H)t\text{-}Bu)(CO)_9(Ph_2P(CH_2)_2PPh_2)]^+BF_4^-$

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Treatment of $R_3(\mu\text{-}H)\{\mu_3\text{-}\eta^2\text{-}C{\equiv}C(t\text{-}Bu)\}(CO)_9$ with $Pt(COD)_2$ (COD = cycloocta-1,5-diene) affords the tetranuclear alkynyl cluster $Ru_3Pt(\mu\text{-}H)\{\mu_4\text{-}\eta^2\text{-}C{\equiv}C(t\text{-}Bu)\}(CO)_9(COD)$ (**4**). Crystal data for **4**: monoclinic, space group $P2_1/n$; a = 11.283 (3), b = 17.843 (2), c = 13.625 (3) Å; β = 94.06 (2)°; V = 2736 (1) Å^3; Z = 4; final R (R_w) values 0.023 (0.029) for 3815 independent observed data ($I > 3.0\sigma(I)$). **4** has an "out-of-plane" spiked-triangular metal framework with a platinum atom bonded to an equilateral Ru_3 triangle via one Ru atom (Ru–Ru = 2.791 (1)–2.815 (1), Ru(2)–Pt = 2.645 (1) Å). The $\mu_4\text{-}\eta^2(\perp)$-alkynyl ligand is σ-bonded to the Pt atom and Ru(2) and asymmetrically π-bonded to the remaining two Ru atoms (Ru(1)–C(11) = 2.484 (5), Ru(3)–C(11) = 2.291 (5) Å), which are also bridged by a hydride. The Pt atom is asymmetrically chelated to a COD ligand, which is easily displaced by bis(diphenylphosphino)ethane (dppe) affording two complexes, the hydrido alkynyl $Ru_3Pt(\mu\text{-}H)\{\mu_4\text{-}\eta^2\text{-}C{\equiv}C(t\text{-}Bu)\}(CO)_9(dppe)$ (**6**) and the tautomeric vinylidene cluster $Ru_3Pt(\mu_4\text{-}\eta^2\text{-}C{=}C(H)t\text{-}Bu)(CO)_9(dppe)$ (**11**). Crystal data for **6**: monoclinic, space group $P2_1/n$; a = 13.867 (3), b = 17.725 (2), c = 17.429 (7) Å; β = 92.50 (2)°; V = 4280 (2) Å^3; Z = 4; final R (R_w) values 0.028 (0.032) for 5167 independent observed data ($I > 3.0\sigma(I)$). Crystal data for **11**: monoclinic, space group $C2/c$; a = 47.561 (5), b = 12.176 (2), c = 23.155 (10) Å; β = 118.27 (2)°; V = 11810 (6) Å^3; Z = 8; final R (R_w) values 0.048 (0.056) for 5865 independent observed data ($I > 2.5\sigma(I)$). Complex **6** has a similar Ru_3Pt core (Ru–Ru = 2.792 (1)–2.824 (1), Ru(3)–Pt = 2.681 (1) Å) and $\mu_4\text{-}\eta^2(\perp)$-alkynyl geometry to that found in **4**, except that this ligand is more symmetrically π-bonded to the two hydrido-bridged Ru atoms (Ru(1)–C(11) = 2.396 (6), Ru(2)–C(11) = 2.427 (6) Å). Complex **11** has a $\mu_4\text{-}\eta^2$-vinylidene ligand bonded to a butterfly Ru_3Pt core, with the Pt atom on a wingtip (Ru–Ru = 2.708 (2)–2.823 (2) Å; Pt–Ru = 2.730 (1), 2.792 (1) Å). The vinylidene moiety is σ-bonded to the Pt atom and to two Ru atoms and is π-bonded to the remaining Ru center. Complexes **6** and **11** readily interconvert in solution, with **11** being the thermodynamically favored product. This facile process involves a reversible skeletal rearrangement of the Ru_3Pt core, and kinetic studies imply an intramolecular mechanism. **11** is protonated by HBF_4 along a metal–metal edge, giving the cationic hydrido vinylidene cluster $[Ru_3Pt(\mu\text{-}H)(\mu_4\text{-}\eta^2\text{-}C{=}C(H)t\text{-}Bu)(CO)_9(dppe)]^+BF_4^-$ (**17**). Crystal data for **17**: triclinic, space group $P\bar{1}$; a = 10.189 (4), b = 14.329 (4), c = 15.596 (9) Å; α = 97.70 (4), β = 94.72 (4), γ = 98.75 (3)°; V = 2218 (2) Å^3; Z = 2, final R (R_w) values 0.035 (0.044) for 6293 independent observed data ($I > 3.0\sigma(I)$). The cluster core closely resembles that found in **11**, with a hydride ligand bridging the hinge Ru–Ru vector. Protonation of **6** occurs at the α-carbon of the acetylide affording the alkyne complex $[Ru_3Pt(\mu\text{-}H)(\mu_4\text{-}\eta^2\text{-}HC{\equiv}C(t\text{-}Bu))(CO)_9(dppe)]^+BF_4^-$ (**18**). **18** irreversibly isomerizes to **17** in solution.

Introduction

There is continuing interest in the structural chemistry[1] and reactivity[2,3] of unsaturated hydrocarbyl ligands that are coordinated to several metal atom sites, since these systems may provide models for reactive species and in-

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