Consequently, the only Ga–As bond length comparison possible is with those found in cyclic species containing four-coordinate Ga and As atoms; the distance in 3 at 2.626 (1) Å is longer than any of the Ga–As lengths in such compounds (see preceding discussion and cited references). The mean As–Si bond length at 2.367 Å lies close to the essentially equal values of 2.358 Å in 1 and 2.363 Å in 2, whereas the mean Ga–C bond length at 1.997 Å is identical with that of 1.997 Å in 2 but longer than that of 1.966 Å in 1. The Ga–Cl bond length at 2.242 (1) Å is significantly shorter than the means of 2.411–2.432 Å in the $\overline{\text{Ga–As–Ga–Cl}}$ rings of 1, 4, and 6. Intramolecular nonbonded interactions between substituents at As and Ga are minimized by a combination of bond angle deformation and rotation around the As–Ga bond. Thus, enlargement of the Cl–Ga–C and C–Ga–C angles (mean 116.4°), due at least in part to electronic effects, results in steric compression at the arsenic atom (mean Si–As–Si angle 106.06° < mean Ga–As–Si angle 112.70°). Rotation around the Ga–As bond aids in producing approximately equidistant C···C separations of ca. 4.0 Å between the carbon atoms in each of the CH_2 groups at Ga and those in pairs of Me groups of the $SiMe_3$ substituents at As.

Conclusions

The facile preparation of compound 1 adds another member to the growing list of mixed-bridge compounds involving the heavier elements of groups III and V. In addition, we believe it is significant that it has been clearly demonstrated that the $\overline{\text{Ga–As–Ga–Cl}}$ ring of 1 is easily converted to the $\overline{\text{Ga–As–Ga–As}}$ ring of 2. This demonstrates the feasibility of using the same methodology to prepare compounds containing the $\overline{\text{Ga–As–Ga–E}}$ ring (E = N, P, Sb). Moreover, the fact that adduct 3 was isolated from the 1:1 mole ratio reaction between $(Me_3CCH_2)_2GaCl$ and $(Me_3Si)_3As$ and that it could not be readily converted to 1 or 2 give some indication that as the bulk of the ligands on gallium increases, dehalosilylation occurs less readily and the adduct is not necessarily an intermediate in the formation of 1 and 2.

Acknowledgment. Financial support for this work by the Office of Naval Research is gratefully acknowledged.

Registry No. 1, 137396-24-8; 2, 137396-25-9; 3, 137396-26-0; $(Me_3CCH_2)_2GaCl$, 113976-09-3; $(Me_3Si)_3As$, 17729-30-5; $LiAs(SiMe_3)_2$, 76938-15-3.

Supplementary Material Available: Tables of hydrogen atom coordinates and isotropic thermal parameters, anisotropic temperature factors, and complete lists of interatomic distances and angles, including torsion angles, for 1–3, as well as equations of least-squares planes through groups of atoms for 1 (18 pages); listings of observed and calculated structure amplitudes for 1–3 (87 pages). Ordering information is given on any current masthead page.

Synthesis, Characterization, and Reaction Chemistry of New Trifluoromethanesulfonato Complexes of Rhodium and Iridium: Formation of Cationic Rh–Pt and Ir–Pt Heterobinuclear Complexes with Bridging Chloride Ligands

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Reactions of $(\eta^5\text{-}C_5Me_5)M(PMe_3)(Cl)_2$ (M = Rh, 1; M = Ir, 2) with excess AgOTf in CH_2Cl_2 give bis(triflate) complexes $(\eta^5\text{-}C_5Me_5)M(PMe_3)(OTf)_2$ (M = Rh, 3; M = Ir, 4). Complexes 3 and 4 undergo facile reactions with CH_3CN affording bis(acetonitrile) complexes $[(\eta^5\text{-}C_5Me_5)M(PMe_3)(CH_3CN)_2]^{2+}[OTf]_2^-$ (M = Rh, 5; M = Ir, 6). Reactions of $(\eta^5\text{-}C_5Me_5)Rh(PMe_3)(OTf)_2$ (3) with *cis*-$Pt(Cl)_2(PR_3)_2$ ($(PR_3)_2 = Ph_2P(CH_2)_3PPh_2$, 7; $PR_3 = PPh_3$, 8) generate heterobinuclear Rh–Pt complexes $[(\eta^5\text{-}C_5Me_5)(PMe_3)Rh(\mu\text{-}Cl)_2Pt(PR_3)_2]^{2+}[OTf]_2^-$ (9, 11). Likewise, reactions of $(\eta^5\text{-}C_5Me_5)Ir(PMe_3)(OTf)_2$ (4) with *cis*-$Pt(Cl)_2(PR_3)_2$ (7, 8) result in the formation of heterobinuclear Ir–Pt complexes $[(\eta^5\text{-}C_5Me_5)(PMe_3)Ir(\mu\text{-}Cl)_2Pt(PR_3)_2]^{2+}[OTf]_2^-$ (10, 12). An unambiguous structural assignment for the heterobinuclear bridging chloride complexes 9–12 has been established by an X-ray diffraction study on complex $[(\eta^5\text{-}C_5Me_5)(PMe_3)Ir(\mu\text{-}Cl)_2Pt(Ph_2P(CH_2)_3PPh_2)]^{2+}[OTf]_2^-$ (10).

Introduction

Transition-metal complexes containing a coordinated triflate ligand have been studied extensively during the past two decades and are a subject of current interest.[1] It is only in the past ten years that the utilization of coordinated triflate precursors in synthesis has become prevalent. Although many triflate complexes of rhodium and iridium are known, to the best of our knowledge, rhodium and iridium triflate complexes involving the pentamethylcyclopentadienyl ligand or its analogues have not yet been reported. This relatively late development of these types of rhodium and iridium triflate complexes is surprising in view of the established value of triflate complexes as versatile and important reagents in mechanistic studies and organometallic synthesis. Therefore, we undertook the design and synthesis of new complexes with the anticipation that newly developed triflate complexes of rhodium and iridium might serve as potentially valuable

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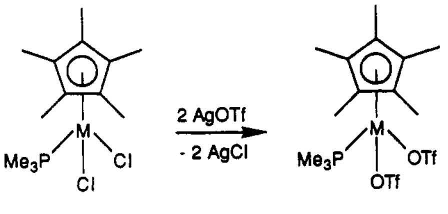
synthons thereby adding a new dimension to their chemistry.

In this work, we wish to report (a) the first examples of pentamethylcyclopentadienyl bis(triflate) complexes of rhodium and iridium $(\eta^5\text{-}C_5Me_5)M(PMe_3)(OTf)_2$ (M = Rh, Ir), (b) the reaction chemistry of these newly prepared triflate complexes with CH_3CN and bis(chloro) platinum complexes *cis*-$Pt(Cl)_2(PR_3)_2$, and (c) the crystal structure determination of a new heterobinuclear Ir–Pt compound $[(\eta^5\text{-}C_5Me_5)(PMe_3)Ir(\mu\text{-}Cl)_2Pt(Ph_2P(CH_2)_3PPh_2)]^{2+}[OTf]_2^-$.

Results and Discussion

Synthesis of Bis(triflate) Complexes $(\eta^5\text{-}C_5Me_5)M(PMe_3)(OTf)_2$ (M = Rh, Ir). $^{31}P\{^1H\}$ NMR monitoring of the reaction between $(\eta^5\text{-}C_5Me_5)Rh(PMe_3)(Cl)_2$ (1)[2] and AgOTf (5.0 equiv) in CH_2Cl_2 at room temperature indicates within 1 h the clean formation of a new product with a resonance at 10.12 ppm (d, $J_{P\text{-}Rh}$ = 144.5 Hz). When this heterogeneous reaction mixture was stirred for 3–6 h, the signal at 10.12 ppm began to disappear as a new major complex with a resonance at 2.19 ppm (d, $J_{P\text{-}Rh}$ = 136.6 Hz) gradually appeared. After 20–40 h the signal at 10.12 ppm diminished and the $^{31}P\{^1H\}$ NMR spectrum of the reaction displayed, in addition to the signal at 2.19 ppm, numerous unidentifiable resonances in the range 6–12 ppm.

Efforts, therefore, were concentrated on the isolation of the first product. In a preparative-scale experiment, reaction of dichloride complex 1 with AgOTf (5.0 equiv) in CH_2Cl_2 at room temperature for 40 min, followed by filtration and CH_2Cl_2/Et_2O precipitation, affords $(\eta^5\text{-}C_5Me_5)Rh(PMe_3)(OTf)_2$ (**3**) as an analytically pure, orange, microcrystalline solid in 86% yield (eq 1). $(\eta^5\text{-}C_5Me_5)Ir(PMe_3)(OTf)_2$ (**4**) is prepared from $(\eta^5\text{-}C_5Me_5)Ir(PMe_3)(Cl)_2$ (**2**)[2] and AgOTf analogously to **3**. Workup gave **4** as an analytically pure, bright yellow, microcrystalline solid in 83% yield (eq 1).



(1)

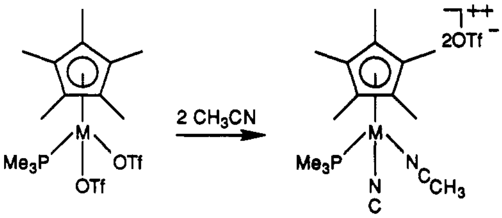
1 M = Rh
2 M = Ir

3 M = Rh
4 M = Ir

Both **3** and **4** are thermally stable and can be stored under a nitrogen or argon atmosphere for long periods of time. Exposure to atmospheric moisture leads to rapid decomposition. The $\eta^5\text{-}C_5Me_5$ ring is a stable ligand which imparts good solubility to its complexes and also acts as a useful NMR probe due to its strong intensity in the ^1H NMR spectrum. The strong $\eta^5\text{-}C_5Me_5$–metal bond and the high lability of the triflate ligand in **3** and **4** should allow versatile reactions to occur. These new complexes are characterized by IR and NMR (^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, ^{19}F) spectroscopy and by microanalysis. In the IR spectra (CD_2Cl_2 solution) the asymmetric sulfonyl stretching frequencies at 1317 and 1324 cm^{-1} characteristic of a coordinated triflate ligand are observed for **3** and **4**, respectively. There is no absorption band present in the range 1235–1288 cm^{-1} attributed to an ionic triflate group.[1a]

Accordingly, we also attempted to synthesize $(\eta^5\text{-}C_5Me_5)M(PMe_3)(Cl)(OTf)$ (M = Rh, Ir) by treating $(\eta^5\text{-}C_5Me_5)M(PMe_3)(Cl)_2$ with 1.0 equiv of AgOTf. Although numerous reaction conditions were examined, such as the utilization of different solvents and reaction temperatures, isolation of the desired products was not successful.

Reaction of $(\eta^5\text{-}C_5Me_5)M(PMe_3)(OTf)_2$ (M = Rh, Ir) with CH_3CN. Bis(triflate) complex **3** was generated in situ as described above. After the precipitated AgCl and excess AgOTf were filtered off, CH_3CN was added to the filtrate. The color of the solution changed from orange to bright yellow instantly. The reaction was worked up after 1 h to give $[(\eta^5\text{-}C_5Me_5)Rh(PMe_3)(CH_3CN)_2]^{2+}[OTf]_2^-$ (**5**) in 83% isolated yield as an analytically pure, yellow microcrystalline solid (eq 2). $[(\eta^5\text{-}C_5Me_5)Ir(PMe_3)(CH_3CN)_2]^{2+}[OTf]_2^-$ (**6**) was prepared from $(\eta^5\text{-}C_5Me_5)Ir(PMe_3)(Cl)_2$ (**2**), AgOTf, and CH_3CN analogously to **5**. Workup gave **6** as an analytically pure, pale yellow, microcrystalline solid in 88% isolated yield (eq 2).



(2)

3 M = Rh
4 M = Ir

5 M = Rh
6 M = Ir

Bis(acetonitrile) complexes **5** and **6** are characterized by IR and NMR (^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, ^{19}F) spectroscopy and by microanalysis. In the IR thin-film spectra, the observation of asymmetric sulfonyl stretching frequencies at 1273 cm^{-1} (**5**) and 1262 cm^{-1} (**6**) is consistent with the presence of ionic triflate groups. In the ^1H NMR spectra, the presence of two coordinated CH_3CN ligands is indicated by doublets due to phosphorus coupling at δ 2.57 (d, $J_{H\text{-}P}$ = 1.0 Hz) and δ 2.77 (d, $J_{H\text{-}P}$ = 1.0 Hz) for **5** and **6**, respectively. Complexes **5** and **6** are thermally stable, and it may be inferred that both of the electron-donating ligands $\eta^5\text{-}C_5Me_5$ and PMe_3 stabilize these highly positively charged complexes.

Reaction of $(\eta^5\text{-}C_5Me_5)M(PMe_3)(OTf)_2$ (M = Rh, Ir) with *cis*-$Pt(Cl)_2(PR_3)_2$. In order to further develop the synthetic potential of these newly prepared, stable bis(triflate) complexes, we sought to investigate their reactions with transition-metal compounds. We anticipated that complexes **3** and **4**, by virtue of the superior nucleofugality of the triflate ligands, might function as transition-metal Lewis acids $[(\eta^5\text{-}C_5Me_5)M(PMe_3)]^{2+}$ which could interact easily with Lewis bases such as bidentate *cis*-$Pt(Cl)_2(PR_3)_2$ via the chloride ligands to afford heterobinuclear adducts.

Bis(triflate) rhodium complex $(\eta^5\text{-}C_5Me_5)Rh(PMe_3)(OTf)_2$ (**3**) was combined with 1.0 equiv of bis(chloro)platinum complex *cis*-$Pt(Cl)_2(Ph_2P(CH_2)_3PPh_2)$ (**7**)[3] in CH_2Cl_2 in a 5-mm NMR tube. Upon shaking, the reaction mixture immediately became homogeneous. The occurrence of a reaction was suggested by the precipitation of orange-yellow microcrystalline solids after a few seconds. After 1 h at room temperature, the solvent was removed and the solid was redissolved in CD_3NO_2 for NMR analysis. In a preparative-scale experiment, the heterobinuclear bridging chloride complex $[(\eta^5\text{-}C_5Me_5)(PMe_3)Rh(\mu\text{-}$

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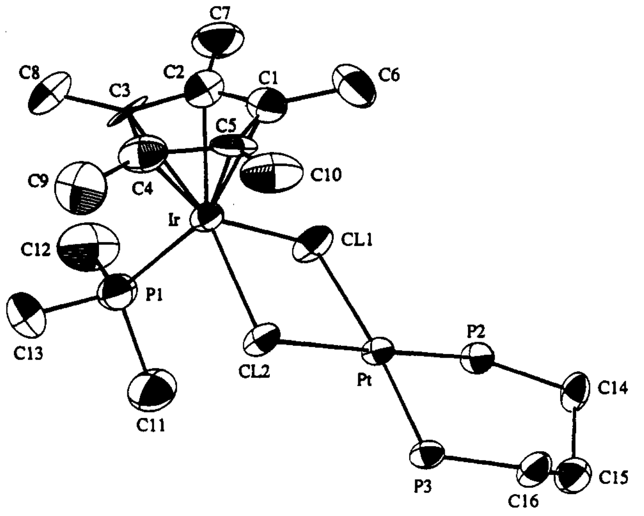

Figure 1. Simplified ORTEP representation of the cation of **10**. The phenyl rings, hydrogen atoms, and triflate anions are omitted for clarity.

$Cl)_2Pt(Ph_2P(CH_2)_3PPh_2)]^{2+}[OTf]_2^-$ (**9**) was isolated in 86% yield as an analytically pure, orange-yellow solid (Scheme I). The structure of **9** was established by IR and mutinuclear (^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, ^{19}F) NMR spectroscopy and by microanalysis. In the ^1H NMR spectrum, the $P(CH_2)_3P$ chemical shifts are the most diagnostic spectroscopic evidence for the formation of the doubly chloride-bridged, heterobinuclear complex. These cyclic $P(CH_2)_3P$ protons appear, as expected, as three sets of broad mutiplets, with low intensities in approximately a 4:1:1 ratio at δ 3.15–2.68 (2 PC*H*H′ and 2 PCH*H*′), 2.68–2.28 (PCC*H*H′CP), and 2.28–1.89 (PCCH*H*′CP). This is consistent with the structural assignment and is different from what is observed in the ^1H NMR spectrum (CD_3NO_2) of the starting material *cis*-$Pt(Cl)_2(Ph_2P(CH_2)_3PPh_2)$ (**7**), which shows two sets of signals at δ 2.74 (m, 2 PCH_2) and 2.07 (m, $PCCH_2$) for the cyclic $P(CH_2)_3P$ protons. Furthermore, the C_5Me_5 proton resonances for complex **9** appear at δ 1.58 (d, J_{H-P} = 3.4 Hz), which is upfield relative to the PMe_3 protons, which resonate at δ 1.77 (d, J_{H-P} = 11.5 Hz). This is contrary to what we have observed for mononuclear complexes such as $(\eta^5\text{-}C_5Me_5)M(PMe_3)(Cl)_2$ (M = Rh, **1**; M = Ir, **2**), $(\eta^5\text{-}C_5Me_5)M(PMe)_3(OTf)_2$ (M = Rh, **3**; M = Ir, **4**), and $[(\eta^5\text{-}C_5Me_5)M(PMe_3)(CH_3CN)_2]^{2+}[OTf]_2^-$ (M = Rh, **5**; M = Ir, **6**); in all of these complexes, the C_5Me_5 proton resonances appear downfield relative to the PMe_3 proton resonances. The upfield shift of the C_5Me_5 proton resonances for **9** is presumably due to the shielding effect of the phenyl rings of the $Ph_2P(CH_2)_3PPh_2$ ligand attached to the Pt atom which are in close proximity. In addition, in the IR spectrum of **9**, the observation of stretching frequencies at 1272 (s), 1224 (m), 1161 (s), and 1030 (s) cm^{-1} (s) is consistent with the presence of ionic triflate groups.[1a]

In analogy to the reaction of the bis(triflate) rhodium complex **3**, interaction of the iridium analogue $(\eta^5\text{-}C_5Me_5)Ir(PMe_3)(OTf)_2$ (**4**) with *cis*-$Pt(Cl)_2(Ph_2P(CH_2)_3PPh_2)$ (**7**) results in an 87% isolated yield of the related adduct $[(\eta^5\text{-}C_5Me_5)(PMe_3)Ir(\mu\text{-}Cl)_2Pt(Ph_2P(CH_2)_3PPh_2)]^{2+}[OTf]_2^-$ (**10**) as yellow crystals (Scheme I). Likewise, reaction of *cis*-$Pt(Cl)_2(PPh_3)_2$ (**8**) with **3** and **4** generates $[(\eta^5\text{-}C_5Me_5)(PMe_3)Rh(\mu\text{-}Cl)_2Pt(PPh_3)_2]^{2+}[OTf]_2^-$ (**11**) and $[(\eta^5\text{-}C_5Me_5)(PMe_3)Ir(\mu\text{-}Cl)_2Pt(PPh_3)_2]^{2+}[OTf]_2^-$ (**12**) in 87% and 74% isolated yield as orange-yellow and yellow crystals, respectively (Scheme I). These complexes are characterized by IR and NMR (^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, ^{19}F) spectroscopy and by microanalysis.

Table I. Summary of Crystallographic Data for $[(\eta^5\text{-}C_5Me_5)(PMe_3)Ir(\mu\text{-}Cl)_2Pt(Ph_2P(CH_2)_3PPh_2)]^{2+}[OTf]_2^-$ (10)

molecular formula	$C_{42}H_{50}Cl_2F_6IrO_6P_3PtS_2$
mol wt	1380.10
cryst system	monoclinic
space group	$P2_1/n$ (No. 1014)
temp of collcn, °C	16 (1)
cell constants	
a, Å	12.062 (1)
b, Å	20.776 (3)
c, Å	19.772 (2)
β, deg	95.09 (1)
V, $Å^3$	4922.56
Z	4
d_{calcd}, g/cm^3	1.862
cryst dimens, mm	0.30 × 0.20 × 0.12
radiation (λ, Å)	Cu (1.540 56)
data collcn method	$\theta/2\theta$
scan speed, deg/min	variable
range/indices (*h*, *k*, *l*)	0 to 14, 0 to 24, -23 to 22
no. of reflcns between std	1 X-ray h
tot. unique data	8366
no. of obsd data, $I > 3\sigma(I)$	6602
abs coeff (μ), cm^{-1}	136.954
min transm factor	0.54
max transm factor	0.99
no. of variables	568
$R = \sum(\|\|F_o\| - \|F_c\|\|)/\sum(F_o)$	0.0484
$R_w = \sum(\|F_o\| - \|F_c\|)w^{1/2}/\sum(F_o)w^{1/2}$	0.0522
goodness of fit	1.01
$\Delta\rho$(max), e/$Å^3$	1.430, 0.8 Å from S1 atom

Table II. Selected Bond Lengths (Å) in 10

Pt–Cl(1)	2.396 (3)	P(2)–C(14)	1.81 (1)
Pt–Cl(2)	2.398 (2)	P(3)–C(16)	1.79 (1)
Pt–P(2)	2.244 (3)	C(1)–C(2)	1.48 (2)
Pt–P(3)	2.245 (3)	C(1)–C(5)	1.34 (2)
Ir–Cl(1)	2.452 (3)	C(1)–C(6)	1.47 (2)
Ir–Cl(2)	2.443 (2)	C(2)–C(3)	1.42 (2)
Ir–P(1)	2.300 (3)	C(2)–C(7)	1.50 (2)
Ir–C(1)	2.25 (1)	C(3)–C(4)	1.49 (2)
Ir–C(2)	2.13 (1)	C(3)–C(8)	1.44 (2)
Ir–C(3)	2.214 (9)	C(4)–C(5)	1.54 (2)
Ir–C(4)	2.17 (1)	C(4)–C(9)	1.51 (2)
Ir–C(5)	2.22 (1)	C(5)–C(10)	1.48 (2)
P1–C(11)	1.80 (1)	C(14)–C(15)	1.54 (2)
P1–C(12)	1.78 (2)	C(15)–C(16)	1.52 (2)
P1–C(13)	1.78 (2)		

Table III. Selected Bond Angles (deg) in 10

Cl(1)–Pt–Cl(2)	83.08 (8)	C(2)–C(1)–C(5)	109 (1)
Cl(1)–Pt–P(2)	91.57 (9)	C(2)–C(1)–C(6)	126 (1)
Cl(1)–Pt–P(3)	174.5 (1)	C(5)–C(1)–C(6)	125 (1)
Cl(2)–Pt–P(2)	173.8 (1)	C(1)–C(2)–C(3)	110 (1)
Cl(2)–Pt–P(3)	91.58 (9)	C(1)–C(2)–C(7)	124 (1)
P(2)–Pt–P(3)	93.7 (1)	C(3)–C(2)–C(7)	125 (1)
Cl(1)–Ir–Cl(2)	81.01 (7)	C(2)–C(3)–C(4)	105 (1)
Cl(1)–Ir–P(1)	90.3 (1)	C(2)–C(3)–C(8)	128 (1)
Cl(2)–Ir–P(1)	90.4 (1)	C(4)–C(3)–C(8)	126 (1)
Pt–Cl(1)–Ir	97.25 (9)	C(3)–C(4)–C(5)	106 (1)
Pt–Cl(2)–Ir	97.43 (8)	C(3)–C(4)–C(9)	126 (1)
Ir–P(1)–C(11)	115.4 (5)	C(5)–C(4)–C(9)	127 (1)
Ir–P(1)–C(12)	114.5 (6)	C(1)–C(5)–C(4)	109 (1)
Ir–P(1)–C(13)	114.9 (6)	C(1)–C(5)–C(10)	129 (1)
C(11)–P(1)–C(12)	103.0 (9)	C(4)–C(5)–C(10)	122 (1)
C(11)–P(1)–C(13)	101.9 (8)	P(2)–C(14)–C(15)	114.3 (8)
C(12)–P(1)–C(13)	106 (1)	C(14)–C(15)–C(16)	110.8 (9)
Pt–P(2)–C(14)	116.2 (4)	P(3)–C(16)–C(15)	117.4 (9)
Pt–P(3)–C(16)	116.2 (4)		

X-ray Crystallographic Study of 10. An unambiguous structural assignment for the heterobinuclear bridging chloride complexes **9–12** has been established by an X-ray diffraction study on complex **10**. The simplified ORTEP representation of the cation is shown in Figure 1. X-ray data are summarized in Table I. Selected bond lengths, Scheme I

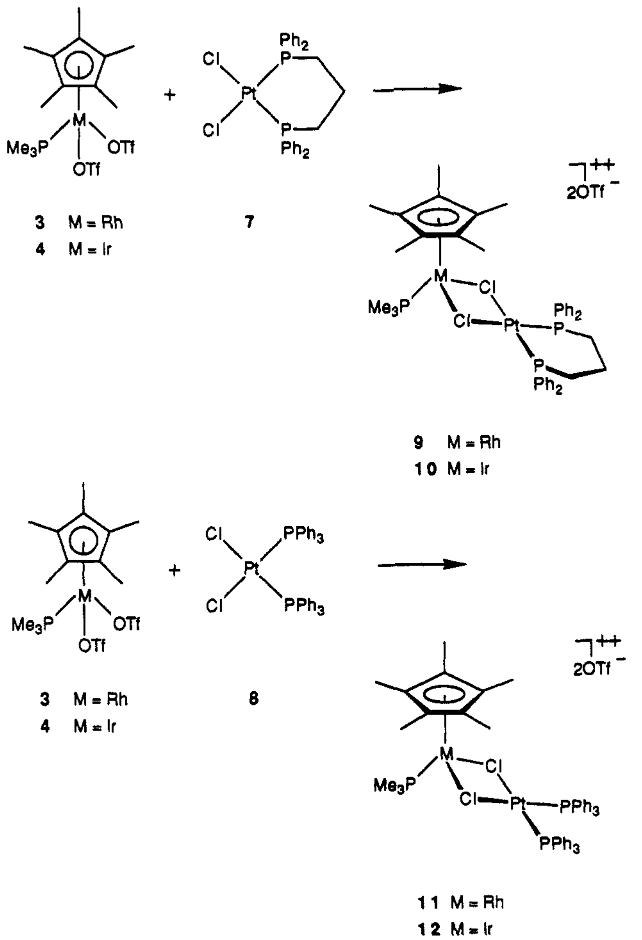

Table IV. Atomic Coordinates and Equivalent Isotropic Thermal Parameters of Non-Hydrogen Atoms in 10[a]

atom	x	y	z	B, Å^2
Pt	0.21854 (4)	0.13763 (2)	0.34763 (2)	2.517 (7)
Ir	0.43872 (4)	0.25654 (2)	0.37812 (2)	2.987 (8)
Cl(1)	0.3947 (2)	0.1470 (1)	0.4133 (1)	4.10 (5)
Cl(2)	0.2737 (2)	0.2375 (1)	0.2997 (1)	3.42 (5)
S(1)	0.4583 (4)	0.3060 (2)	0.0160 (2)	6.35 (9)
S(2)	0.6901 (4)	0.0201 (2)	0.1732 (2)	7.2 (1)
P(1)	0.5503 (3)	0.2160 (2)	0.2996 (2)	4.69 (7)
P(2)	0.1866 (2)	0.0415 (1)	0.3941 (1)	2.97 (5)
P(3)	0.0593 (2)	0.1362 (1)	0.2794 (1)	2.91 (5)
F(1)	0.555 (1)	0.2073 (6)	0.0766 (6)	10.1 (3)
F(2)	0.382 (1)	0.2142 (6)	0.0854 (6)	12.5 (4)
F(3)	0.439 (1)	0.1848 (5)	−0.0083 (6)	12.7 (4)
F(4)	0.583 (1)	−0.0446 (6)	0.0768 (6)	14.0 (4)
F(5)	0.547 (1)	0.0523 (6)	0.0758 (7)	16.8 (4)
F(6)	0.715 (2)	0.024 (1)	0.0543 (9)	23.9 (8)
O(1)	0.487 (1)	0.3408 (6)	0.0782 (6)	8.2 (3)
O(2)	0.548 (1)	0.3073 (6)	−0.0288 (5)	9.7 (3)
O(3)	0.351 (1)	0.3136 (8)	−0.0164 (9)	13.8 (5)
O(4)	0.7217 (8)	0.0862 (5)	0.1803 (6)	7.1 (3)
O(5)	0.772 (1)	−0.0251 (6)	0.182 (1)	13.3 (5)
O(6)	0.595 (1)	0.0030 (8)	0.2125 (8)	13.1 (4)
C(1)	0.396 (1)	0.3014 (7)	0.4763 (6)	4.7 (3)
C(2)	0.516 (1)	0.2886 (6)	0.4734 (7)	4.8 (3)
C(3)	0.560 (1)	0.3281 (5)	0.4232 (7)	5.1 (3)
C(4)	0.461 (1)	0.3598 (6)	0.3866 (7)	5.4 (3)
C(5)	0.361 (1)	0.3407 (6)	0.4250 (5)	4.6 (3)
C(6)	0.323 (1)	0.2725 (9)	0.5241 (7)	6.8 (4)
C(7)	0.586 (1)	0.2498 (8)	0.5252 (7)	6.5 (4)
C(8)	0.674 (1)	0.3385 (8)	0.4117 (8)	6.8 (4)
C(9)	0.463 (2)	0.4074 (6)	0.3288 (9)	7.5 (5)
C(10)	0.249 (1)	0.3686 (7)	0.4078 (8)	7.0 (4)
C(11)	0.488 (1)	0.1538 (8)	0.2450 (8)	7.2 (4)
C(12)	0.676 (1)	0.179 (1)	0.336 (1)	8.6 (5)
C(13)	0.592 (1)	0.273 (1)	0.2395 (8)	7.8 (4)
C(14)	0.0422 (9)	0.0207 (5)	0.4005 (6)	3.5 (2)
C(15)	−0.031 (1)	0.0227 (6)	0.3323 (6)	4.2 (3)
C(16)	−0.0536 (9)	0.0918 (6)	0.3098 (6)	3.8 (2)
C(17)	0.2503 (9)	0.0361 (5)	0.4803 (5)	3.4 (2)
C(18)	0.337 (1)	−0.0057 (7)	0.4974 (7)	5.8 (3)
C(19)	0.380 (1)	−0.0063 (8)	0.5658 (9)	8.0 (4)
C(20)	0.340 (1)	0.0301 (8)	0.6153 (7)	6.9 (4)
C(21)	0.255 (1)	0.0717 (7)	0.5968 (6)	5.2 (3)
C(22)	0.211 (1)	0.0755 (6)	0.5301 (6)	4.1 (3)
C(23)	0.2452 (9)	−0.0228 (4)	0.3472 (6)	3.3 (2)
C(24)	0.216 (1)	−0.0863 (6)	0.3595 (7)	5.0 (3)
C(25)	0.266 (1)	−0.1358 (6)	0.3264 (8)	6.0 (4)
C(26)	0.342 (1)	−0.1240 (6)	0.2823 (7)	5.3 (3)
C(27)	0.374 (1)	−0.0611 (6)	0.2698 (7)	5.3 (3)
C(28)	0.325 (1)	−0.0109 (5)	0.3029 (6)	4.2 (3)
C(29)	0.082 (1)	0.1053 (5)	0.1965 (5)	3.4 (2)
C(30)	−0.010 (1)	0.0863 (6)	0.1505 (6)	4.4 (3)
C(31)	0.010 (1)	0.0658 (7)	0.0846 (6)	5.9 (3)
C(32)	0.118 (1)	0.0615 (7)	0.0661 (7)	5.9 (4)
C(33)	0.206 (1)	0.0801 (8)	0.1093 (7)	6.2 (4)
C(34)	0.185 (1)	0.1023 (7)	0.1747 (6)	5.1 (3)
C(35)	−0.0007 (8)	0.2159 (5)	0.2673 (5)	3.0 (2)
C(36)	−0.010 (1)	0.2530 (6)	0.3249 (6)	4.7 (3)
C(37)	−0.067 (1)	0.3128 (6)	0.3179 (6)	4.5 (3)
C(38)	−0.112 (1)	0.3333 (6)	0.2555 (7)	4.8 (3)
C(39)	−0.102 (1)	0.2967 (6)	0.1989 (7)	6.6 (3)
C(40)	−0.047 (1)	0.2375 (6)	0.2055 (6)	5.7 (3)
C(41)	0.459 (2)	0.2251 (8)	0.0434 (8)	7.7 (5)
C(42)	0.613 (2)	0.0139 (8)	0.0947 (9)	9.6 (6)

[a] B values for atoms refined anisotropically are given in the form of the isotropic equivalent displacement parameters, defined as $(4/3)[a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab(\cos\gamma)B_{1,2} + ac(\cos\beta)B_{1,3} + bc(\cos\alpha)B_{2,3}]$.

selected bond angles, and atomic coordinates are given in Tables II-IV. The nonbonded Ir···Pt distance in the Ir-(μ-Cl)$_2$Pt bridge is 3.638 Å. The Pt atom exists in a nearly square-planar environment with two bridging chloride ligands and two chelated phosphorus atoms, as indicated by the deviation from the mean plane (maximum deviations: Pt, −0.0398 Å; P(2), 0.0290 Å; P(3), −0.0077 Å; Cl(1), 0.0098 Å; Cl(2), 0.0278 Å). The six-membered ring containing Pt and the $Ph_2P(CH_2)_3PPh_2$ ligand adopts a chairlike conformation. The dihedral angle between the two planes defined by Cl(1)–Ir–Cl(2) and Cl(1)–Pt–Cl(2) is approximately 11°. The two bridging chloride ligands are nearly symmetrically bound to the Pt metal center with a Pt–Cl(1) distance of 2.396 (3) Å, a Pt–Cl(2) distance of 2.398 (2) Å, and a Cl(1)–Pt–Cl(2) angle of 83.08 (8)°, which are comparable to the distances of 2.326 (6) and 2.460 (5) Å of the Pt–Cl bonds and a Cl–Pt–Cl angle of 82.5 (2)° in the doubly chloride-bridged complex $[(C_{12}H_9N_2)Pt]_2(\mu\text{-}Cl)_2$.[4h] The two bridging chloride ligands are also nearly symmetrically bound to the Ir metal center with an Ir–Cl(1) distance of 2.452 (3) Å, an Ir–Cl(2) distance of 2.443 (2) Å, and a Cl(1)–Ir–Cl(2) angle of 81.01 (7)°. These values are comparable to the Ir–Cl distances of 2.456 (3) and 2.449 (3) Å and a Cl–Ir–Cl angle of 79.55 (12)° in the doubly chloride-bridged complex $[(\eta^5\text{-}C_5Me_5)Ir(Cl)]_2(\mu\text{-}Cl)_2$.[4g]

Although a wide variety of homobinuclear, doubly chloride-bridged, transition-metal complexes have been synthesized and characterized,[4] the heterobinuclear analogues $L_mM(\mu\text{-}Cl)_2M'L_n$ are relatively rare.[5] Examples of

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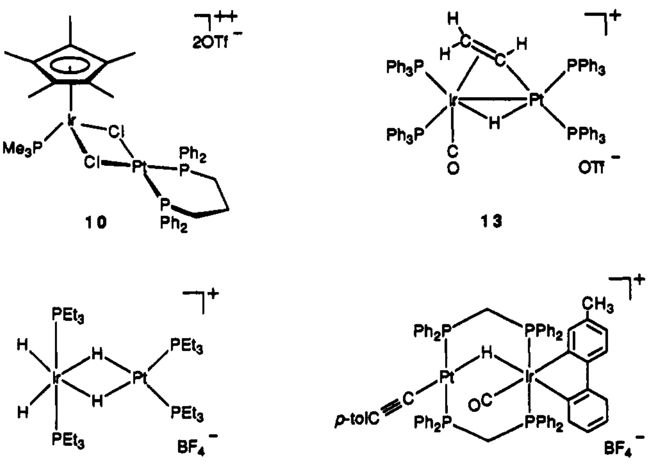
Scheme II



10 13 14 15

heterobinuclear complexes containing both iridium and platinum, either with or without a direct metal-metal bond, are also rather limited. To our knowledge, only three types of heterobinuclear Ir-Pt complexes have been structurally characterized. One is our heterobinuclear Ir-Pt complex 13[6] (Scheme II), which contains a bridging vinyl and a bridging hydride ligand. Another type is Venanzi's Ir-Pt complex 14[7] and its analogues (Scheme II), which contain both terminal and bridging hydride ligands. The other example is Shaw's Ir-Pt complex 15[8] (Scheme II), which also contains a hydride ligand bridging between iridium and platinum metal centers.

Conclusion

We have demonstrated simple and high-yielding preparative routes to bis(triflate) complexes $(\eta^5\text{-}C_5Me_5)M(PMe_3)(OTf)_2$ (M = Rh, 3; M = Ir, 4) from readily available starting materials. Although complexes 3 and 4 are sensitive to atmospheric moisture, these microcrystalline bis(triflate) complexes can be manipulated easily using drybox techniques and stored under an inert-gas atmosphere for months without noticeable decomposition. This study has also provided examples which demonstrate the synthetic versatility of the bis(triflate) complexes 3 and 4 as precursors to a number of products in substitution reactions. The highly labile triflate ligands in complexes 3 and 4 can be displaced cleanly and rapidly by a neutral CH_3CN molecule to give bis(acetonitrile) complexes $[(\eta^5\text{-}C_5Me_5)M(PMe_3)(CH_3CN)_2]^{2+}[OTf]_2^-$ (M = Rh, 5; M = Ir, 6). In addition, the bis(chloro)platinum complexes *cis*-$Pt(Cl)_2(PR_3)_2$ (7, 8) act as bidentate Lewis bases utilizing two nucleophilic chloride ligands to bind the highly positively charged rhodium and iridium metal centers of $(\eta^5\text{-}C_5Me_5)M(PMe_3)(OTf)_2$ leading to the formation of heterobinuclear chloride-bridged Rh-Pt and Ir-Pt complexes (9-12). As mentioned previously, although a wide variety of homobinuclear, doubly chloride-bridged, transition-metal complexes have been reported, the heterobinuclear analogues $L_mM(\mu\text{-}Cl)_2M'L_n$ are relatively rare. We attribute the successful synthesis of these heterobinuclear products to the superior leaving group ability of the triflate ligands, which permits complexes 3 and 4 to behave as transition-metal Lewis acids.

Experimental Section

Materials and Measurements. All reactions were conducted under a dry nitrogen atmosphere using Schlenk techniques, unless otherwise noted. IR spectra were recorded on a Mattson Polaris FT-IR spectrometer. All NMR spectra were recorded on a Varian XL-300 spectrometer. ^1H NMR spectra were recorded at 300 MHz, and all chemical shifts are reported in ppm relative to internal tetramethylsilane or the proton resonance resulting from incomplete deuteration of the NMR solvent. ^{13}C NMR spectra were recorded at 75 MHz, and all chemical shifts are reported in ppm relative to the carbon of the deuterated NMR solvent. ^{31}P NMR spectra were recorded at 121 MHz, and all chemical shifts are reported in ppm relative to external 85% H_3PO_4 at 0.0 ppm. ^{19}F NMR spectra were recorded at 282 MHz, and all chemical shifts are reported upfield relative to external $CFCl_3$ at 0.0 ppm. Elemental analyses were conducted by Atlantic Microlab, Inc., of Norcross, GA. Melting points were determined in evacuated capillaries and were not corrected.

Solvents were purified as follows: CH_3NO_2 and CH_2Cl_2 were purified by literature procedures[9] and were distilled from CaH_2; ether was purified by literature procedures[9] and was distilled from Na/benzophenone; CH_3CN and CD_3NO_2 were distilled from CaH_2; CD_2Cl_2 was vacuum transferred from CaH_2. All solvents were freeze-thaw-pump degassed three times before use.

Reagents were obtained as follows: Silver triflate (Aldrich) was recrystallized from diethyl ether and vacuum dried; *cis*-$Pt(Cl)_2(PPh_3)_2$ (Aldrich) was used as received; $(\eta^5\text{-}C_5Me_5)Rh(PMe_3)(Cl)_2$ (1),[2] $(\eta^5\text{-}C_5Me_5)Ir(PMe_3)(Cl)_2$ (2),[2] and *cis*-$Pt(Cl)_2(Ph_2P(CH_2)_3PPh_2)$ (7)[3] were prepared by literature procedures.

Preparation of $(\eta^5\text{-}C_5Me_5)Rh(PMe_3)(OTf)_2$ (3). A Schlenk flask was charged with $(\eta^5\text{-}C_5Me_5)Rh(PMe_3)(Cl)_2$ (1) (0.160 g, 0.415 mmol), AgOTf (0.534 g, 2.078 mmol), and a magnetic stirring bar and was capped with a rubber septum. Freshly distilled, degassed CH_2Cl_2 (60 mL) was added via cannula. The heterogeneous mixture was stirred at room temperature for 40 min and then was immediately filtered under nitrogen. The filtrate was concentrated to ca. 3 mL, and diethyl ether (ca. 20 mL) was added with stirring to effect precipitation. The volume was concentrated to ca. 10 mL, and then the remaining solvent was removed via cannula. The precipitate was washed with ether (ca. 10 mL), dried under vacuum, and stored in an argon atmosphere glovebox. This gave 3 as an orange, microcrystalline solid (0.219 g, 0.358 mmol, 86%): mp 216-218 °C dec; IR (cm^{-1}, CD_2Cl_2) $\nu_{asym,SO}$ 1317 s; ^1H NMR (δ, CD_2Cl_2) 1.70 (d, J_{H-P} = 3.6 Hz, C_5Me_5), 1.62 (d, J_{H-P} = 12.0 Hz, PMe_3); $^{13}C\{^1H\}$ NMR (ppm, CD_2Cl_2) 119.45 (q, J_{C-F} = 318.0 Hz, 2 CF_3SO_3), 99.96 (dd, J_{C-Rh} = 9.1 Hz, J_{C-P} = 2.5 Hz, C_5Me_5), 13.87 (d, J_{C-P} = 29.9 Hz, PMe_3), 10.12 (s, C_5Me_5); $^{31}P\{^1H\}$ NMR (ppm, CD_2Cl_2) 10.12 (d, J_{P-Rh} = 144.5 Hz, P-Rh); ^{19}F NMR (ppm, CD_2Cl_2) -78.36 (s). Anal. Calcd for $C_{15}H_{24}F_6O_6PRhS_2$: C, 29.42; H, 3.95. Found: C, 29.21; H, 4.00.

Preparation of $(\eta^5\text{-}C_5Me_5)Ir(PMe_3)(OTf)_2$ (4). This compound was prepared from $(\eta^5\text{-}C_5Me_5)Ir(PMe_3)(Cl)_2$ (2) (0.180 g, 0.379 mmol), AgOTf (0.488 g, 1.899 mmol), and CH_2Cl_2 (60 mL) by a procedure identical to that given for 3. The solvent was removed from the filtrate under vacuum. This gave a bright yellow solid, which was washed with diethyl ether (2 × 10 mL). The supernatant was removed via cannula. The solid was dried under vacuum and stored in an argon atmosphere glovebox. This gave 4 as a yellow, microcrystalline solid (0.220 g, 0.314 mmol, 83%): mp 209-211 °C dec; IR (cm^{-1}, CD_2Cl_2) $\nu_{asym,SO}$ 1324 s; ^1H NMR (δ, CD_2Cl_2) 1.71 (d, J_{H-P} = 2.2 Hz, C_5Me_5), 1.70 (d, J_{H-P} = 11.5 Hz, PMe_3); $^{13}C\{^1H\}$ NMR (ppm, CD_2Cl_2) 118.90 (q, J_{C-F} = 316.9 Hz, 2 CF_3SO_3), 92.42 (d, J_{C-P} = 2.5 Hz, C_5Me_5), 13.99 (d, J_{C-P} = 37.5 Hz, PMe_3), 10.21 (s, C_5Me_5); $^{31}P\{^1H\}$ NMR (ppm, CD_2Cl_2) -9.53 (s, P-Ir); ^{19}F NMR (ppm, CD_2Cl_2) -78.12 (s). Anal. Calcd for $C_{15}H_{24}F_6IrO_6PS_2$: C, 25.68; H, 3.45. Found: C, 25.61; H, 3.56.

Preparation of $[(\eta^5\text{-}C_5Me_5)Rh(PMe_3)(CH_3CN)_2]^{2+}[OTf]_2^-$ (5). A Schlenk flask was charged with $(\eta^5\text{-}C_5Me_5)Rh(PMe_3)(Cl)_2$

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(1) (0.081 g, 0.210 mmol), AgOTf (0.268 g, 1.043 mmol), and a magnetic stirring bar and was capped with a rubber septum. Freshly distilled, degassed CH_2Cl_2 (30 mL) was added via cannula. The heterogeneous mixture was stirred at room temperature for 40 min and then was immediately filtered under nitrogen. To this filtrate was added CH_3CN (1 mL) by syringe. The color of the solution changed from yellow-orange to bright yellow instantly. The solution was stirred for 1 h and concentrated under vacuum, and diethyl ether was added to effect precipitation. The solid was collected by filtration, washed with ether, and dried under vacuum to give **5** (0.121 g, 0.174 mmol, 83%) as a yellow, microcrystalline solid: mp 156–159 °C dec; IR (cm^{-1}, thin film) ν_{CN} 2320 m, 2293 m, ν_{OTf} 1273 s, 1226 m, 1160 s, 1031 s; ^1H NMR (δ, CD_3NO_2) 2.57 (d, J_{H-P} = 1.0 Hz, 2 CH_3CN), 1.86 (d, J_{H-P} = 3.8 Hz, C_5Me_5), 1.76 (d, J_{H-P} = 12.0 Hz, PMe_3); $^{13}C\{^1H\}$ NMR (ppm, CD_3NO_2) 128.66 (d, J = 5.6 Hz, 2 $CH_3\mathit{C}N$), 122.29 (q, J_{C-F} = 319.6 Hz, 2 CF_3SO_3), 105.28 (dd, J_{C-Rh} = 7.0 Hz, J_{C-P} = 2.0 Hz, C_5Me_5), 14.53 (d, J_{C-P} = 32.0 Hz, PMe_3), 9.87 (s, $C_5\mathit{Me}_5$), 4.12 (s, 2 $\mathit{C}H_3CN$); $^{31}P\{^1H\}$ NMR (ppm, CD_3NO_2) 10.41 (d, J_{P-Rh} = 121.3 Hz, P–Rh); ^{19}F NMR (ppm, CD_3NO_2) −78.49 (s). Anal. Calcd for $C_{19}H_{30}F_6N_2O_6PRhS_2$: C, 32.86; H, 4.35. Found: C, 32.93; H, 4.28.

Preparation of $[(\eta^5\text{-}C_5Me_5)Ir(PMe_3)(CH_3CN)_2]^{2+}[OTf]_2^-$ (6). This compound was prepared from $(\eta^5\text{-}C_5Me_5)Ir(PMe_3)(Cl)_2$ (**2**) (0.080 g, 0.169 mmol), AgOTf (0.217 g, 0.845 mmol), CH_2Cl_2 (30 mL), and CH_3CN (1 mL) by a procedure identical to that given for **5**. Workup gave **6** as a pale yellow, microcrystalline solid (0.116 g, 0.148 mmol, 88%): mp 200–203 °C dec; IR (cm^{-1}, thin film) ν_{CN} 2326 m, 2297 m, ν_{OTf} 1262 s, 1224 m, 1154 s, 1030 s; ^1H NMR (δ, CD_3NO_2) 2.77 (d, J_{H-P} = 1.0 Hz, 2 CH_3CN), 1.91 (d, J_{H-P} = 2.3 Hz, C_5Me_5), 1.86 (d, J_{H-P} = 11.7 Hz, PMe_3); $^{13}C\{^1H\}$ NMR (ppm, CD_3NO_2) 125.38 (s, 2 $CH_3\mathit{C}N$), 122.33 (q, J_{C-F} = 320.4 Hz, 2 CF_3SO_3), 98.63 (d, J_{C-P} = 2.1 Hz, C_5Me_5), 14.26 (d, J_{C-P} = 39.6 Hz, PMe_3), 9.42 (s, $C_5\mathit{Me}_5$), 4.37 (s, 2 $\mathit{C}H_3CN$); $^{31}P\{^1H\}$ NMR (ppm, CD_3NO_2) −23.60 (s, P–Ir); ^{19}F NMR (ppm, CD_3NO_2) −78.52 (s). Anal. Calcd for $C_{19}H_{30}F_6IrN_2O_6PS_2$: C, 29.12; H, 3.86. Found: C, 29.22; H, 3.83.

Preparation of $[(\eta^5\text{-}C_5Me_5)(PMe_3)Rh(\mu\text{-}Cl)_2Pt(Ph_2P(CH_2)_3PPh_2)]^{2+}[OTf]_2^-$ (9). A. NMR-Monitored Experiment. In an argon atmosphere glovebox, a 5-mm NMR tube was charged with $(\eta^5\text{-}C_5Me_5)Rh(PMe_3)(OTf)_2$ (**3**) (0.032 g, 0.052 mmol) and was capped with a rubber septum. The NMR tube was taken out of the glovebox. A needle, connected to a vacuum line, was inserted through the rubber septum. CH_2Cl_2 (0.7 mL) was injected by syringe. Another NMR tube was charged with *cis*-$Pt(Cl)_2(Ph_2P(CH_2)_3PPh_2)$ (**7**) (0.035 g, 0.052 mmol), capped with a rubber septum, and attached to a vacuum line. The CH_2Cl_2 solution of **3** was then transferred by syringe into the NMR tube containing **7**. The NMR tube was removed from the vacuum line and shaken vigorously, resulting in a homogeneous solution. After a few seconds, an orange-yellow microcrystalline solid precipitated, and the liquid phase also remained orange-yellow. The mixture was kept at room temperature for 1 h, and then solvent was removed under vacuum. CD_3NO_2 (0.7 mL) was then added to effect complete dissolution for analysis by $^{31}P\{^1H\}$ NMR spectroscopy.

B. In a preparative-scale experiment, in an argon atmosphere glovebox, a Schlenk flask was charged with $(\eta^5\text{-}C_5Me_5)Rh(PMe_3)(OTf)_2$ (**3**) (0.038 g, 0.062 mmol), *cis*-$Pt(Cl)_2(Ph_2P(CH_2)_3PPh_2)$ (**7**) (0.042 g, 0.062 mmol), and a magnetic stirring bar and was capped with a rubber septum. The flask was taken out of the glovebox and was attached to a vacuum line. CH_2Cl_2 (55 mL) was added via cannula. The resulting solution was stirred at room temperature for 1 h and then was filtered under nitrogen. The filtrate was concentrated under vacuum, and diethyl ether was added with stirring to effect precipitation. The solid was filtered out, washed with ether, and dried under vacuum to give **9**·$0.15CH_2Cl_2$ (0.069 g, 0.053 mmol, 86%) as an orange-yellow, microcrystalline solid: mp >260 °C; IR (cm^{-1}, KBr) ν_{OTf} 1272 s, 1224 m, 1161 s, 1030 s; ^1H NMR (δ, CD_3NO_2) 7.90–7.45 (m, 4 C_6H_5), 5.44 (s, CH_2Cl_2), 3.15–2.68 (br m, 2 PCH_2), 2.68–2.28 (br m, $PCC\mathit{H}H'CP$), 2.28–1.89 (br m, $PCCH\mathit{H}'CP$), 1.77 (d, J_{H-P} = 11.5 Hz, PMe_3), 1.58 (d, J_{H-P} = 3.4 Hz, C_5Me_5); $^{13}C\{^1H\}$ NMR (ppm, CD_3NO_2) phenyl carbons at 135.13–123.92 (m), 122.47 (q, J_{C-F} = 320.6 Hz, 2 CF_3SO_3), 103.67 (dd, J_{C-Rh} = 7.5 Hz, J_{C-P} = 2.5 Hz, C_5Me_5), 55.33 (s, CH_2Cl_2), 24.02 (t, J_{C-P} = 24.5 Hz, 2 PCH_2), 19.53 (t, J_{C-P} = 2.6 Hz, $PC\mathit{C}H_2$), 14.40 (d, J_{C-P} = 31.9 Hz, PMe_3), 9.85 (s, $C_5\mathit{Me}_5$); $^{31}P\{^1H\}$ NMR (ppm, CD_3NO_2) 7.90 (d, J_{P-Rh} = 140.9 Hz, P–Rh), −1.73 (s with ^{195}Pt satellites, J_{P-Pt} = 3446 Hz, 2 P–Pt); ^{19}F NMR (ppm, CD_3NO_2) −78.48 (s). Anal. Calcd for $C_{42}H_{50}Cl_2F_6O_6P_3PtRhS_2 \cdot 0.15CH_2Cl_2$: C, 38.84; H, 3.89. Found: C, 38.53; H, 3.85.

Preparation of $[(\eta^5\text{-}C_5Me_5)(PMe_3)Ir(\mu\text{-}Cl)_2Pt(Ph_2P(CH_2)_3PPh_2)]^{2+}[OTf]_2^-$ (10). A. NMR-Monitored Experiment. The sample was prepared in a 5-mm NMR tube from $(\eta^5\text{-}C_5Me_5)Ir(PMe_3)(OTf)_2$ (**4**) (0.022 g, 0.031 mmol), *cis*-$Pt(Cl)_2(Ph_2P(CH_2)_3PPh_2)$ (**7**) (0.021 g, 0.031 mmol), and CH_2Cl_2 (0.7 mL) by a procedure identical to that given above. The resulting mixture became homogeneous. After a few minutes, a pale yellow microcrystalline solid precipitated, and the liquid phase also remained pale yellow. The mixture was kept at room temperature for 1 h, and then the solvent was removed under vacuum. CD_3NO_2 (0.7 mL) was then added to effect complete dissolution for analysis by $^{31}P\{^1H\}$ NMR spectroscopy.

B. In a preparative-scale experiment, complex **10** was prepared from $(\eta^5\text{-}C_5Me_5)Ir(PMe_3)(OTf)_2$ (**4**) (0.080 g, 0.114 mmol), *cis*-$Pt(Cl)_2(Ph_2P(CH_2)_3PPh_2)$ (**7**) (0.077 g, 0.114 mmol), and CH_2Cl_2 (100 mL) by a procedure identical to that given for **9**. Workup gave **10**·$0.15CH_2Cl_2$ (0.138 g, 0.099 mmol, 87%) as a pale yellow, microcrystalline solid: mp >260 °C; IR (cm^{-1}, KBr) ν_{OTf} 1272 s, 1224 m, 1156 s, 1030 s; ^1H NMR (δ, CD_3NO_2) 7.90–7.45 (m, 4 C_6H_5), 5.44 (s, CH_2Cl_2), 3.16–2.71 (br m, 2 PCH_2), 2.71–2.31 (br m, $PCC\mathit{H}H'CP$), 2.31–1.97 (br m, $PCCH\mathit{H}'CP$), 1.87 (d, J_{H-P} = 11.2 Hz, PMe_3), 1.61 (d, J_{H-P} = 2.1 Hz, C_5Me_5); $^{13}C\{^1H\}$ NMR (ppm, CD_3NO_2) phenyl carbons at 135.04–124.36 (m), 122.49 (q, J_{C-F} = 320.5 Hz, 2 CF_3SO_3), 96.69 (d, J_{C-P} = 2.5 Hz, C_5Me_5), 55.33 (s, CH_2Cl_2), 23.75 (t, J_{C-P} = 24.5 Hz, 2 PCH_2), 19.56 (t, J_{C-P} = 3.4 Hz, $PC\mathit{C}H_2$), 14.15 (d, J_{C-P} = 38.5 Hz, PMe_3), 9.48 (s, $C_5\mathit{Me}_5$); $^{31}P\{^1H\}$ NMR (ppm, CD_3NO_2) 0.43 (s with ^{195}Pt satellites, J_{P-Pt} = 3425 Hz, 2 P–Pt), −14.87 (s, P–Ir); ^{19}F NMR (ppm, CD_3NO_2) −78.48 (s). Anal. Calcd for $C_{42}H_{50}Cl_2F_6IrO_6P_3PtS_2 \cdot 0.15CH_2Cl_2$: C, 36.35; H, 3.64. Found: C, 35.98; H, 3.61.

Preparation of $[(\eta^5\text{-}C_5Me_5)(PMe_3)Rh(\mu\text{-}Cl)_2Pt(PPh_3)_2]^{2+}[OTf]_2^-$ (11). A. NMR-Monitored Experiment. The sample was prepared in a 5-mm NMR tube from $(\eta^5\text{-}C_5Me_5)Rh(PMe_3)(OTf)_2$ (**3**) (0.020 g, 0.033 mmol), *cis*-$Pt(Cl)_2(PPh_3)_2$ (**8**) (0.026 g, 0.033 mmol), and CD_2Cl_2 (0.7 mL) by a procedure identical to that given above. The homogeneous mixture was kept at room temperature, and the reaction was periodically monitored by $^{31}P\{^1H\}$ NMR spectroscopy. A $^{31}P\{^1H\}$ NMR spectrum showed that all starting materials were consumed within 30 min.

B. In a preparative-scale experiment, complex **11** was prepared from $(\eta^5\text{-}C_5Me_5)Rh(PMe_3)(OTf)_2$ (**3**) (0.100 g, 0.163 mmol), *cis*-$Pt(Cl)_2(PPh_3)_2$ (**8**) (0.129 g, 0.163 mmol), and CH_2Cl_2 (30 mL) by a procedure identical to that given for **9**. Workup gave **11** (0.199 g, 0.142 mmol, 87%) as a yellow, microcrystalline solid. IR (cm^{-1}, CD_2Cl_2) ν_{OTf} 1270 s, 1225 m, 1158 s, 1031 s; ^1H NMR (δ, CD_3NO_2) 7.70–7.30 (m, 6 C_6H_5), 1.79 (d, J_{H-P} = 11.5 Hz, PMe_3), 1.64 (d, J_{H-P} = 3.4 Hz, C_5Me_5); $^{13}C\{^1H\}$ NMR (ppm, CD_3NO_2) phenyl carbons at 136.03 (t, J_{C-P} = 5.6 Hz), 134.16 (s), 130.43 (t, J_{C-P} = 5.8 Hz), 126.55 (dd, J_{C-P} = 70.5, 2.9 Hz), triflate carbon not observed, 103.75 (dd, J_{C-Rh} = 7.7 Hz, J_{C-P} = 2.7 Hz, C_5Me_5), 14.57 (d, J_{C-P} = 32.0 Hz, PMe_3), 9.90 (s, $C_5\mathit{Me}_5$); $^{31}P\{^1H\}$ NMR (ppm, CD_3NO_2) 14.74 (s with ^{195}Pt satellites, J_{P-Pt} = 3790 Hz, 2 P–Pt), 7.27 (d, J_{P-Rh} = 142.4 Hz, P–Rh); ^{19}F NMR (ppm, CD_3NO_2) −78.77 (s). Anal. Calcd for $C_{51}H_{54}Cl_2F_6O_6P_3PtRhS_2$: C, 43.66; H, 3.88. Found: C, 43.76; H, 3.90.

Preparation of $[(\eta^5\text{-}C_5Me_5)(PMe_3)Ir(\mu\text{-}Cl)_2Pt(PPh_3)_2]^{2+}[OTf]_2^-$ (12). A. NMR-Monitored Experiment. The sample was prepared in a 5-mm NMR tube from $(\eta^5\text{-}C_5Me_5)Ir(PMe_3)(OTf)_2$ (**4**) (0.022 g, 0.031 mmol), *cis*-$Pt(Cl)_2(PPh_3)_2$ (**8**) (0.024 g, 0.030 mmol), and CD_2Cl_2 (0.7 mL) by a procedure identical to that given above. The homogeneous mixture was kept at room temperature, and the reaction was periodically monitored by $^{31}P\{^1H\}$ NMR spectroscopy. A $^{31}P\{^1H\}$ NMR spectrum showed that all starting materials were consumed within 30 min.

B. In a preparative-scale experiment, complex **12** was prepared from $(\eta^5\text{-}C_5Me_5)Ir(PMe_3)(OTf)_2$ (**4**) (0.060 g, 0.086 mmol), *cis*-$Pt(Cl)_2(PPh_3)_2$ (**8**) (0.066 g, 0.084 mmol), and CH_2Cl_2 (15 mL) by a procedure identical to that given for **9**. Workup gave **12** (0.093 g, 0.062 mmol, 74%) as a pale yellow, microcrystalline solid. IR (cm^{-1}, CD_2Cl_2) ν_{OTf} 1269 s, 1225 m, 1158 s, 1031 s; ^1H NMR (δ, CD_2Cl_2) 7.63–7.23 (m, 6 C_6H_5), 1.85 (d, J_{H-P} = 11.0 Hz, PMe_3), 1.58 (d, J_{H-P} = 2.1 Hz, C_5Me_5); $^{13}C\{^1H\}$ NMR (ppm, CD_2Cl_2) phenyl carbons at 134.67 (t, J_{C-P} = 5.2 Hz), 133.38 (s), 129.59 (t, J_{C-P} = 6.0 Hz), 124.54 (dd, J_{C-P} = 71.9, 2.6 Hz), triflate carbon not observed, 95.62 (d, J_{C-P} = 2.7 Hz, C_5Me_5), 14.19 (d, J_{C-P} = 38.6, PMe_3), 9.46 (s, C_5Me_5); $^{31}P\{^1H\}$ NMR (ppm, CD_2Cl_2) 15.54 (s with ^{195}Pt satellites, J_{P-Pt} = 3774 Hz, 2 P–Pt), −16.00 (s, P–Ir); ^{19}F NMR (ppm, CD_2Cl_2) −78.97 (s). Anal. Calcd for $C_{51}H_{54}Cl_2F_6IrO_6P_3PtS_2$: C, 41.05; H, 3.65. Found: C, 40.36; H, 3.60.

Single-Crystal X-ray Diffraction Study of 10. Orange crystals of **10** were obtained by vapor diffusion of Et_2O into a CH_3NO_2 solution. A suitable crystal with a dimension of 0.30 × 0.20 × 0.12 mm was mounted on a glass fiber and was coated with epoxy cement for preliminary data collection on a Enraf-Nonius CAD-4 diffractometer. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using setting angles of 25 reflections in the range $20° < 2\theta < 28°$. The monoclinic cell parameters and calculated volume are as follows: a = 12.062 (1) Å, b = 20.776 (3) Å, c = 19.722 (2) Å, and V = 4922.56 $Å^3$. The space group was determined to be $P2_1/n$ (No. 1014).

The data were collected at a temperature of 16 (1) °C using a variable scan rate. A total of 9082 reflections were collected, of which 8366 were unique and not systematically absent. As a check on crystal and electronic stability, two representative reflections were measured every 200 reflections.

Lorentz and polarization corrections, and an empirical absorption correction based upon a series of ψ scans, were applied to the data. Inspection of the intensity standards revealed an overall reduction of 12.5% of the original intensity. The data were corrected for this decay. The structure was solved by the Patterson heavy-atom method. The structure was refined in full-matrix least squares, where the function minimized was $\sum w(|F_o| - |F_c|)^2$, with a weight of 1.0 for all observed reflections. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atom positions were calculated and were not refined. Scattering factors, and $\Delta f'$ and $\Delta f''$ values were taken from the literature.[10] Anomalous dispersion effects were included in F_c.[11] All calculations were performed on a VAX 8300 computer with the SDP/VAX package.[12]

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Registry No. 1, 80298-79-9; 2, 80298-81-3; 3, 137363-15-6; 4, 137363-16-7; 5, 137363-18-9; 6, 137363-20-3; 7, 59329-00-9; 8, 15604-36-1; 9, 137393-29-4; 10, 137363-26-9; $10 \cdot 0.15CH_2Cl_2$, 137363-27-0; 11, 137363-22-5; 12, 137363-24-7.

Supplementary Material Available: A table of anisotropic thermal parameters for **10** (3 pages); a listing of calculated and observed structure factors for **10** (23 pages). Ordering information is given on any current masthead page.

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$[ReH_2(CO)_2(PMe_2Ph)_3]^+$, a Dihydride Complex with Classical and Nonclassical Tautomeric Forms in Equilibrium

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Reactions of $[ReH_3(CO)(PMe_2Ph)_3]$ (**1**) with PMe_2Ph or CO in refluxing THF give the monohydride complexes *trans*-$ReH(CO)(PMe_2Ph)_4$ (**2**) and *cis,mer*-$[ReH(CO)_2(PMe_2Ph)_3]$ (**3**), respectively. Protonation of **2** with $HBF_4 \cdot OMe_2$ in CH_2Cl_2 at 298 K gives the classical dihydride complex $[ReH_2(CO)_2(PMe_2Ph)_3]^+$ (**4**), while protonation of **3** in CD_2Cl_2 at 193 K results in an equilibrium mixture of the classical dihydride complex $[ReH_2(CO)_2(PMe_2Ph)_3]^+$ (**5a**) and its nonclassical dihydrogen tautomer $[Re(\eta^2\text{-}H_2)(CO)_2(PMe_2Ph)_3]^+$ (**5b**). The η^2-HD isotopomer of **5b**, formed by protonation of the corresponding monodeuteride complex, shows a $^1J_{HD}$ value of 31 Hz in the ^1H NMR spectrum. Variable-temperature ^1H NMR equilibrium studies for the conversion of **5a** to **5b** produce the thermodynamic parameters $\Delta H = 1.7 \pm 0.4$ kcal mol^{-1} and $\Delta S = 8 \pm 3$ cal mol^{-1} K^{-1}. The lower limit of $\Delta G^{\neq}$ for the conversion of **5b** to **5a** at 223 K is estimated to be 11.5 ± 0.3 kcal mol^{-1}.

Introduction

Transition-metal η^2-dihydrogen complexes have received much recent attention.[1] Complexes on the borderline between classical, $M(H)_2$, and nonclassical, $M(\eta^2\text{-}H_2)$, behavior are of particular interest. In most cases, a pair of interconverting tautomers are found,[2–6] one of which is unambiguously classical, with $r(H \cdots H) > 1.65$ Å, and the other nonclassical, with $r(H-H) < 1$ Å.

Very recently Howard et al.[7] have shown by neutron diffraction that $ReH_7\{P(p\text{-tolyl})_3\}_2$ has an H···H distance of 1.357 Å, an intermediate value which lies between the

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