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Weak Rh←H–C Interactions. Molecular Structure of [*trans*-Rh(CO)(8-methylquinoline)$(PPh_3)_2$]BF_4

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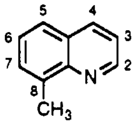
Treatment of [Rh(CO)Cl$(ER_3)_2$] with the appropriate silver salt AgX in CH_3CN affords the solvento complexes [*trans*-Rh(CO)(CH_3CN)$(ER_3)_2$]X (**4a**, E = P, R = Ph, X = BF_4; **4b**, E = P, R = Cy, X = CF_3SO_3; **4c**, E = As, R = Ph, X = BF_4). Only **4a** and **4c** react at room temperature with 8-methylquinoline (mqH) to give the stable cationic complexes [*trans*-Rh(CO)(mqH)$(EPh_3)_2$]BF_4 (**5a**, E = P; **5b**, E = As). NMR characterization of **5** in solution suggests the presence of a quinoline methyl group weakly interacting with the rhodium center. The X-ray crystal structure determination of **5a** confirmed the presence of a quinoline molecule coordinated through the N atom with the methyl group lying above the coordination plane. **5a** crystallizes in the triclinic system, space group $P\bar{1}$, with a = 12.348 (2) Å, b = 14.424 (3) Å, c = 15.545 (3) Å, α = 77.36 (2)°, β = 81.22 (2)°, γ = 89.28 (2)°, and Z = 2. The Rh···C(11) separation (3.118 Å) and Rh···H(11a) separation (ca. 2.21 Å) are in agreement with weak M···H–C interactions.

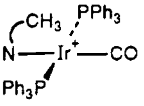
Chemically inert C–H bonds of saturated carbon centers can be effectively activated through "agostic" interactions,[1] wherein the C–H bonds act as ligands toward transition-metal centers. It is generally agreed that covalent agostic C–H→M interactions lead to lower ν(C–H) stretching frequencies, short M–H distances, and, more noticeably, reduced $^1J(^1H^{13}C)$ coupling constants and *high-field* shifts of the ^1H NMR signals.[1,2] Weaker interactions, however, are suggested in the presence of *low-field* ^1H shifts (with $\Delta\delta$ values in the range 0.3–3.3 ppm) and *normal* $^1J(^1H^{13}C)$ values.[3] Following earlier studies by Deeming et al.[4-6] to evaluate weak M←H–C bonds, Pregosin and co-workers[3,7-9] have developed an empirical method mainly based on $^nJ(M^1H)$ and $^nJ(M^{13}C)$ coupling constants.

Unsubstituted[3,4,10] (or 2-substituted[5,6]) 8-alkylquinolines appeared to be ideal ligands to bring one or more C–H bonds of the alkyl substituent sufficiently close to the metal such that weak interactions could develop.

We have recently[11] shown that 8-methylquinoline (mqH) readily replaces the acetonitrile ligand in [*trans*-Ir(CO)(CH_3CN)$(PPh_3)_2$]PF_6 (**1**), affording the cationic [*trans*-Ir(CO)(mqH)$(PPh_3)_2$]PF_6 (**2**), which features an η^1-mqH molecule. As a result, the N coordination locates the 8-methyl group above the coordination plane, leading to an Ir–H distance of ca. 2.25 Å.



mqH



2

We thereafter decided to extend the iridium chemistry to the Rh metal ion (^{103}Rh, $I = {}^1/_2$, natural abundance 100%), thus introducing a valuable probe to better understand the nature of the M←H–C interaction.

Results and Discussion

The isoelectronic Rh analogues of **2** have been prepared by modifying a synthetic procedure reported by Reed and Venanzi[12] for [Rh(CO)(CH_3CN)L_2]BF_4 (L_2 = 2,11-bis((diphenylphosphino)methyl)benzo[*c*]phenanthrene). Treatment of [Rh(CO)Cl$(ER_3)_2$] (E = P, R = Ph (**3a**), Cy (**3b**); E = As, R = Ph (**3c**)) with the appropriate silver salt AgX in CH_3CN afforded complexes **4** as yellow air-stable solids (eq 1).

$$[\mathrm{Rh(CO)Cl(ER_3)_2}] + \mathrm{AgX} \xrightarrow{\mathrm{CH_3CN}} \underset{\mathbf{4a-c}}{[\mathit{trans}\text{-}\mathrm{Rh(CO)(CH_3CN)(ER_3)_2}]\mathrm{X}} \quad (1)$$

4a, E = P, R = Ph, X = BF_4; **4b**, E = P, R = Cy, X = CF_3SO_3; **4c**, E = As, R = Ph, X = BF_4

The new species[12] have good solubility in chlorinated solvents and acetone and have been proved to be 1:1 electrolytes in CH_2Cl_2 solution.

A room-temperature reaction of [*trans*-Rh(CO)(CH_3CN)$(PPh_3)_2$]BF_4 (**4a**) and mqH in dichloromethane gave rise to [*trans*-Rh(CO)(mqH)$(PPh_3)_2$]BF_4 (**5a**) in high yield. The bright yellow product was characterized by spectroscopic methods (see Experimental Section) and by X-ray crystallography (vide infra).

Deeming et al.[14] earlier reported the formation of [Rh(CO)(mqH)$(PPh_3)_2$]ClO_4, characterized only by IR and ^1H NMR spectroscopy. The ^1H NMR spectrum of **5a** in CD_2Cl_2 has the same features observed for Deeming's compound. In particular, the mqH methyl resonance appears as a sharp singlet at 3.39 ppm, ca. 0.6 ppm downfield with respect to free[11] mqH. At −80 °C the signal broadens, but no J(RhH) or J(PH) value is resolved. On the other end, the $^{13}C\{^1H\}$ NMR signal corresponding to the CH_3 group of coordinated mqH shows coupling to ^{103}Rh, appearing as a broad doublet (^nJ(RhC) = 1.8 Hz) at 19.9 ppm

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[13] The cationic [*trans*-Rh(CO)(CH_3CN)$(PPh_3)_2$][$HC(SO_2CF_3)_2$] has been recently prepared by a completely different method: Siedle, A. R.; Gleason, W. B.; Newmark, R. A.; Skarjune, R. P.; Lyon, P. A.; Markell, C. G.; Hodgson, K. O.; Roe, A. L. *Inorg. Chem.* **1990**, *29*, 1667.

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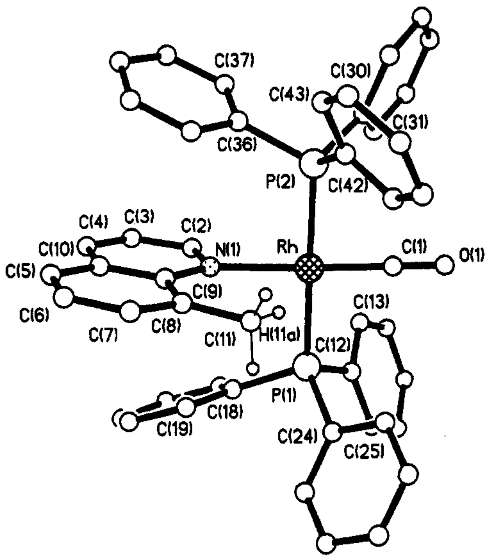
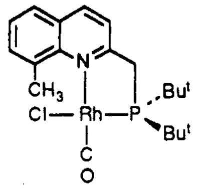


Figure 1. PLUTO drawing of the cation of [*trans*-Rh(CO)(8-methylquinoline)$(PPh_3)_2$]BF_4 (**5a**) with the numbering scheme.

($\Delta\delta(^{13}C)$ = 2.3 ppm) in CD_2Cl_2. Better resolution was not achieved even at −80 °C.

^{13}C coupling to ^{103}Rh in **5a** could be realized in two different ways, leading to coupling constants of different order. A weak direct interaction between the proximate methyl group and the Rh atom would imply a formal $^2J(^{103}Rh^{13}C)$ value. A coupling mechanism operating through the quinoline framework would give a $^4J(^{103}Rh^{13}C)$ value instead. Since observation of long-range rhodium–carbon coupling is not common, and despite the absence of *J*(PH) and *J*(RhH), we suggest the presence in **5a** of a very weak Rh←H–C interaction. The normal value of $^1J(^1H^{13}C)_{av}$ at 126 Hz found for the methyl group of **5a** could be considered as supportive evidence for such a weak interaction. However, this cannot be a conclusive evidence by itself, since a fluxional agostic methyl group would give a similar value for the averaged $^1J(^1H^{13}C)$. Interestingly, [Rh(CO)Cl(mqp)] (mqp = ((8-methyl-2-quinolyl)methyl)di-*tert*-butylphosphine)



wherein the interaction between the 8-CH_3 group and the Rh atom is less geometrically favored, does not show Rh coupling to the methyl group.[6] The trans relationship of the phosphine ligands in **5a** is confirmed by the presence of a single doublet (^1J(RhP) = 131 Hz) in the ^{31}P NMR spectrum.

Whereas [*trans*-Rh(CO)(CH_3CN)$(PCy_3)_2$]CF_3SO_3 (**4b**), incorporating two phosphine ligands with a large cone angle, failed to react with mqH even at high temperature,[15] [*trans*-Rh(CO)(CH_3CN)$(AsPh_3)_2$]BF_4 (**4c**) readily reacts with mqH to give [*trans*-Rh(CO)(mqH)$(AsPh_3)_2$]BF_4 (**5b**). Complex **5b** has ^1H and ^{13}C NMR shifts remarkably similar to those seen for **5a**. In particular, the ^{13}C methyl resonance has the same shift and a similar coupling constant (^nJ(RhC) = 2.0 Hz).

Table I. Crystal Data for [*trans*-Rh(CO)(mqH)$(PPh_3)_2$]BF_4•2.5$CHCl_3$

formula	$C_{49.5}H_{41.5}BCl_{7.5}F_4NOP_2Rh$
fw	1183.94
space group	$P\bar{1}$
a, Å	12.348 (2)
b, Å	14.424 (3)
c, Å	15.545 (3)
α, deg	77.36 (2)
β, deg	81.22 (2)
γ, deg	89.28 (2)
V, Å^3	2669.3 (9)
Z	2
ρ_{calc}, g cm^{-3}	1.470
T, °C	22 ± 2
λ, Å	0.710 69
μ(Mo Kα), cm^{-1}	8.01
scan mode	ω–2θ
2θ range, deg	3.0–50.0
no. of unique data	9354
no. of data obsd	5798 ($I > 3\sigma(I)$)
no. of params refined	630
$R(F_o)^a$	0.055
$R_w(F_o)^b$	0.060
S^c	1.39

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$; $w^{-1} = \sigma(F_o)^2 + 0.002(F_o)^2$. [c] Goodness of fit $= [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

Table II. Selected Bond Distances (Å), Angles (deg), and Torsion Angles (deg) for [*trans*-Rh(CO)(mqH)$(PPh_3)_2$]BF_4•2.5$CHCl_3$

	Bond Distances		
Rh–P(1)	2.337 (2)	Rh–P(2)	2.344 (2)
Rh–C(1)	1.811 (7)	Rh–N(1)	2.135 (5)
Rh–H(11a)	2.21 (1)	Rh–C(11)	3.118 (9)
N(1)–C(9)	1.376 (9)	N(1)–C(2)	1.310 (8)
C(3)–C(4)	1.342 (12)	C(2)–C(3)	1.392 (10)
C(6)–C(7)	1.378 (13)	C(4)–C(10)	1.397 (10)
C(8)–C(9)	1.416 (10)	C(5)–C(10)	1.410 (13)
C(9)–C(10)	1.429 (9)	C(5)–C(6)	1.314 (18)
C(8)–C(11)	1.470 (10)	C(7)–C(8)	1.379 (13)
C(1)–O(1)	1.145 (18)	C(11)–H(11a)	0.96 (1)
	Angles		
P(1)–Rh–P(2)	176.7 (1)	P(1)–Rh–N(1)	90.6 (1)
P(2)–Rh–N(1)	90.5 (1)	P(1)–Rh–C(1)	89.4 (2)
P(2)–Rh–C(1)	89.2 (2)	C(1)–Rh–N(1)	175.0 (3)
Rh–N(1)–C(2)	108.5 (4)	Rh–N(1)–C(9)	131.9 (4)
Rh–C(1)–O(1)	179.5 (6)	N(1)–C(2)–C(3)	123.9 (7)
C(3)–C(4)–C(10)	120.7 (7)	C(4)–C(10)–C(9)	118.4 (7)
N(1)–C(9)–C(10)	119.1 (6)	N(1)–C(9)–C(8)	121.6 (5)
C(7)–C(8)–C(9)	116.9 (6)	C(6)–C(7)–C(8)	123.6 (9)
C(5)–C(6)–C(7)	120.0 (10)	C(10)–C(5)–C(6)	121.5 (8)
C(7)–C(8)–C(11)	118.5 (7)	C(9)–C(8)–C(11)	124.5 (7)
	Torsion Angles		
N(1)–C(9)–C(8)–C(11)	3.3 (11)		
N(1)–C(9)–C(8)–C(7)	−176.7 (7)		
N(1)–C(9)–C(10)–C(5)	−176.3 (7)		
C(2)–N(1)–C(9)–C(8)	178.3 (6)		
C(4)–C(10)–C(9)–C(8)	−177.7 (7)		
P(1)–Rh–N(1)–C(2)	−85.2 (4)		
P(1)–Rh–N(1)–C(9)	99.3 (6)		
Rh–N(1)–C(9)–C(8)	−6.7 (10)		
Rh–N(1)–C(2)–C(3)	−175.7 (6)		

The molecular structure of **5a**·2.5$CHCl_3$ shows a four-coordinate rhodium atom with trans PPh_3 ligands, a linear carbonyl group (Rh–C(1)–O(1) = 179.5 (6)°), and a mqH molecule coordinated through the nitrogen atom (Figure 1). The deviations from the least-squares plane through Rh, P(1), N(1), P(2), and C(1) (−0.025, 0.036, 0.043, 0.041, and 0.076 Å, respectively) indicate a modest distortion from ideal square planarity. Relevant structural data are

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[15] At room temperature in dichloromethane solution **4b** was recovered unreacted. After 20 h of reflux in benzene a pale yellow solid was obtained upon workup. The product, probably [Rh(CO)$(PCy_3)_2$(OSO_2CF_3)], exhibits ν(CO) at 1950 cm^{-1} (KBr) and $\delta(^{31}P)$ at 38.7 ppm (*J*(RhP) = 117 Hz) in $CDCl_3$. Anal. Calcd for $C_{38}H_{66}F_3O_4SP_2Rh$: C, 54.67; H, 7.24. Found: C, 54.59; H, 7.68.

Table III. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for [*trans*-Rh(CO)(mqH)(PPh$_3$)$_2$]BF$_4$•2.5CHCl$_3$

	x	*y*	*z*	*U*(eq)[a]		*x*	*y*	*z*	*U*(eq)[a]
				Complex					
Rh	278 (1)	3208 (1)	2147 (1)	41 (1)*	C(25)	1683 (7)	5549 (5)	1286 (6)	79 (3)*
P(1)	2103 (1)	3682 (1)	2050 (1)	46 (1)*	C(26)	1798 (8)	6521 (6)	1132 (6)	96 (4)*
P(2)	−1518 (1)	2664 (1)	2201 (1)	48 (1)*	C(27)	2481 (8)	6939 (5)	1546 (6)	79 (3)*
N(1)	184 (4)	2658 (3)	3549 (3)	47 (2)*	C(28)	3102 (7)	6374 (5)	2107 (6)	74 (3)*
O(1)	464 (4)	3808 (4)	185 (3)	80 (2)*	C(29)	3005 (5)	5399 (5)	2267 (5)	59 (3)*
C(1)	395 (5)	3573 (5)	945 (5)	54 (3)*	C(30)	−1680 (6)	2001 (5)	1363 (4)	56 (3)*
C(2)	551 (6)	1790 (5)	3676 (4)	55 (3)*	C(31)	−799 (7)	1554 (6)	995 (6)	80 (4)*
C(3)	543 (7)	1195 (5)	4514 (5)	71 (3)*	C(32)	−932 (10)	1022 (7)	397 (7)	105 (5)*
C(4)	114 (7)	1519 (6)	5237 (5)	81 (4)*	C(33)	−1906 (12)	912 (6)	143 (6)	103 (5)*
C(5)	−791 (9)	2800 (9)	5883 (6)	101 (5)*	C(34)	−2805 (10)	1347 (7)	510 (6)	96 (4)*
C(6)	−1151 (9)	3672 (9)	5780 (7)	107 (5)*	C(35)	−2686 (7)	1897 (6)	1098 (5)	72 (3)*
C(7)	−1069 (7)	4249 (7)	4939 (6)	89 (4)*	C(36)	−2100 (5)	1852 (5)	3243 (4)	57 (3)*
C(8)	−613 (6)	3968 (5)	4172 (5)	61 (3)*	C(37)	−2081 (7)	884 (5)	3306 (5)	77 (3)*
C(9)	−233 (5)	3025 (5)	4274 (4)	52 (2)*	C(38)	−2477 (9)	269 (7)	4111 (7)	105 (5)*
C(10)	−301 (6)	2435 (6)	5149 (5)	72 (3)*	C(39)	−2878 (9)	605 (9)	4849 (7)	112 (5)*
C(11)	−551 (7)	4654 (5)	3314 (5)	76 (3)*	C(40)	−2867 (8)	1568 (8)	4791 (5)	100 (4)*
C(12)	3041 (5)	3327 (4)	1164 (4)	49 (2)*	C(41)	−2479 (6)	2207 (6)	3991 (5)	73 (3)*
C(13)	2830 (6)	2510 (5)	901 (5)	66 (3)*	C(42)	−2494 (5)	3620 (5)	2043 (4)	50 (2)*
C(14)	3587 (8)	2190 (6)	289 (6)	88 (4)*	C(43)	−3573 (6)	3508 (5)	2482 (6)	73 (3)*
C(15)	4548 (7)	2673 (6)	−51 (5)	78 (3)*	C(44)	−4261 (7)	4257 (7)	2367 (7)	94 (4)*
C(16)	4767 (6)	3481 (6)	204 (5)	71 (3)*	C(45)	−3930 (7)	5122 (6)	1807 (6)	84 (4)*
C(17)	4018 (5)	3819 (5)	812 (4)	58 (3)*	C(46)	−2864 (7)	5224 (6)	1365 (6)	81 (3)*
C(18)	2719 (5)	3193 (4)	3042 (4)	52 (2)*	C(47)	−2158 (6)	4486 (5)	1503 (5)	69 (3)*
C(19)	2394 (6)	3528 (5)	3819 (5)	62 (3)*	B	1388 (11)	9796 (9)	2298 (8)	94 (5)*
C(20)	2816 (8)	3130 (6)	4591 (5)	78 (3)*	F(1)	312 (7)	9819 (7)	2638 (5)	188 (5)*
C(21)	3563 (8)	2423 (7)	4589 (6)	91 (4)*	F(2)	1588 (7)	10430 (5)	1559 (6)	181 (4)*
C(22)	3878 (7)	2080 (6)	3840 (6)	80 (4)*	F(3)	1686 (9)	8992 (5)	2199 (6)	221 (6)*
C(23)	3453 (6)	2456 (5)	3074 (5)	63 (3)*	F(4)	1908 (9)	10045 (9)	2901 (7)	239 (7)*
C(24)	2296 (5)	4971 (4)	1862 (4)	51 (2)*					
				Solvent Molecules					
C(48)	4363 (9)	9409 (8)	2311 (8)	118 (5)*	Cl(4B)	8256 (14)	8180 (9)	1054 (7)	256 (8)*
Cl(1)	4744 (4)	9445 (3)	1182 (3)	184 (2)*	Cl(5B)	7841 (16)	8411 (20)	2809 (17)	405 (17)*
Cl(2)	4594 (4)	8264 (3)	2899 (3)	205 (3)*	Cl(6B)	9061 (21)	7133 (12)	2395 (22)	436 (21)*
Cl(3)	5167 (4)	10176 (3)	2670 (4)	219 (3)*	C(50)	5005 (35)	4719 (28)	4625 (24)	197 (14)
C(49)	8717 (13)	8162 (10)	2078 (8)	159 (7)*	Cl(7)	6098 (12)	4496 (11)	4872 (11)	263 (6)
Cl(4A)	7978 (18)	7418 (14)	3087 (8)	378 (12)*	Cl(8)	5842 (14)	5612 (11)	3982 (10)	291 (6)
Cl(5A)	7823 (11)	8857 (7)	1700 (10)	219 (7)*	Cl(9)	4453 (12)	5775 (9)	4395 (10)	247 (5)
Cl(6A)	8930 (13)	7297 (11)	1470 (12)	252 (10)*					

[a] Asterisks denote equivalent isotropic *U* values, defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

listed in Tables I–III. The overall structure of the cation is very similar to that reported for 2,[11] the main difference being the P(1)–Rh–P(2) angle of 176.7 (1)° as compared to the corresponding angle of 168.3 (1)° in 2. The Rh–N distance (2.135 (5) Å) is slightly shorter than the same distance in [Rh(Quin)(CO)(PPh$_3$)][16a] (2.162 (6) Å; Quin = 2-carboxyquinolinato) and [Rh(Quin)(CO){P(OPh)$_3$}][16b] (2.145 (5) Å) but longer than that in the Rh(III) species [Rh(CH$_2$Ph)Cl(C$_6$H$_5$N)$_2$(qn)] (qn = 8-carbonylquinolinato; Rh–N = 2.042 (3) Å)[17a] and [Rh(CH$_2$CH$_3$)Cl(C$_6$H$_4$N)$_2$(qn)] (Rh–N = 2.047 (5) Å).[17b] The quinoline fragment is roughly planar and, being in the "upright" position, forms a dihedral angle of 85.6 (1)° with the mean coordination plane. This causes the 8-CH$_3$ group to occupy a pseudoaxial position above the coordination plane, affording a Rh–C(11) distance of 3.118 (9) Å. One of the C–H bonds of the methyl group is therefore correctly positioned to interact with the unsaturated metal center. The Rh–H(11a) separation of 2.21 Å (2.072 Å is the estimated value by using C–H = 1.11 Å) is in fact in the right range for weak M···H interactions.[2,3] The value of ca. 156° for Rh–H(11a)–C(11) angle is well outside the reported range for a "truly agostic" type of bond.[2,10] It is noteworthy that in a number of systems containing remote agostic bonds[3,8,9,18] narrower M–H–C angles are associated with M–H and M–C distances longer than those observed in our case. We must finally note that the rhodium atom is not raised considerably out of the mean plane through N(1), P(1), P(2), and C(1) atoms, the deviation being only 0.065 Å.

Experimental Section

All experiments were performed under a dry nitrogen atmosphere. The ligand 8-methylquinoline (Fluka AG), AgBF$_4$ (Aldrich), and AgCF$_3$SO$_3$ (Aldrich) were used as received. Rh(CO)Cl(EPh$_3$)$_2$[19] (E = P, As) and Rh(CO)Cl(PCy$_3$)$_2$[20] were prepared according to the literature. The NMR spectra were recorded on a Bruker WH 300 spectrometer. Chemical shifts (in ppm) are referenced to internal TMS (^{1}H) and to external 85% H$_3$PO$_4$ (^{31}P). Conductivity measurements were made using an LKB 5300 B Conductolyser conductivity bridge. Analyses were performed by the Microanalytical Laboratory of our department.

[*trans*-Rh(CO)(CH$_3$CN)(PPh$_3$)$_2$]BF$_4$ (4a) and Related Salts. Rh(CO)Cl(PPh$_3$)$_2$ (350 mg, 0.53 mmol) was treated with AgBF$_4$ (110 mg, 0.56 mmol) in CH$_3$CN (15 mL). The suspension was stirred for 2 h in the dark, and then the solid AgCl was filtered. The yellow filtrate was evaporated under reduced pressure, and

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the powdered solid product was redissolved in CH_2Cl_2. Addition of diethyl ether afforded the product as yellow needles (320 mg, 78%). Anal. Calcd for $C_{39}H_{33}BF_4NOP_2Rh$: C, 59.80; H, 4.24; N, 1.79. Found: C, 59.60; H, 4.20; N, 1.46. NMR ($CDCl_3$): ^{31}P, δ 30.5 (d, $J(RhP) = 120$ Hz); ^1H, δ 1.50 (s, CH_3CN). IR (KBr): $\nu(CN)$ 2318 (w), 2292 (w) cm^{-1}; $\nu(CO)$ 1976 (s br) cm^{-1}. Λ_M (10^{-4} M in CH_2Cl_2) = 43.55 Ω^{-1} mol^{-1} cm^2.

The corresponding PCy_3 (**4b**) and $AsPh_3$ (**4c**) derivatives were obtained as described above for **4a** as the $CF_3SO_3^-$ and BF_4^- salts, respectively.

4b: yield 62%. Anal. Calcd for $C_{40}H_{63}F_3NO_4P_2RhS$: C, 54.85; H, 7.25; N, 1.60. Found: C, 54.14; H, 7.99, N, 1.58. NMR ($CDCl_3$): ^{31}P, δ 39.0 (d, $J(RhP) = 113$ Hz); ^1H, δ 2.58 (s, CH_3CN). IR (KBr): $\nu(CN)$ 2308 (w), 2280 (w) cm^{-1}; $\nu(CO)$ 1966 (s) cm^{-1}. Λ_M (10^{-4} M in CH_2Cl_2) = 38.44 Ω^{-1} mol^{-1} cm^2.

4c: yield 80%. Anal. Calcd for $C_{39}H_{33}As_2BF_4NORh \cdot CH_2Cl_2$: C, 53.76; H, 3.82; N, 1.61. Found: C, 53.70; H, 3.80; N, 1.71. ^1H NMR ($CDCl_3$) δ 1.58 (s, CH_3CN). IR (KBr): $\nu(CN)$ 2327 (w), 2284 (w) cm^{-1}; $\nu(CO)$ 1987 (s br) cm^{-1}. Λ_M (10^{-4} M in CH_2Cl_2) = 43.77 Ω^{-1} mol^{-1} cm^2.

[*trans*-Rh(CO)(mqH)(PPh_3)$_2$]BF_4 (5a). Solid mqH (35 μL, 0.26 mmol) was added to a solution of **4a** (150 mg, 0.19 mmol) in CH_2Cl_2 (5 mL). After 3 h of stirring the starting dark yellow solution turned pale yellow. Adding diethyl ether (5 mL) and cooling (−20 °C) afforded **5a** as a yellow crystalline solid (154 mg, 90%). Anal. Calcd for $C_{47}H_{39}BF_4NOP_2Rh$: C, 63.75; H, 4.44; N, 1.58. Found: C, 63.81; H, 4.45; N, 1.56. NMR: ^{31}P ($CDCl_3$), δ 32.0 (d, $J(RhP) = 131$ Hz); ^1H (CD_2Cl_2), δ 8.94 (dd, $J = 5.2$ Hz, $J = 1.7$ Hz, H-2), 7.89 (br d, $J = 8.2$ Hz, H-4), 6.81 (dd, $J = 8.2$ Hz, $J = 5.2$ Hz, H-3), 3.39 (s, 8-CH_3); ^{13}C (CD_2Cl_2), δ 189.7 (dt, $J(RhC) = 70$ Hz, $J(PC) = 16$ Hz, Rh–CO), [152.2, 145.3, 140.2, 134.3, 132.0, 131.0, 128.7, 127.7, 120.8, 9 aromatic C, mqH], [134.04 (t, $J = 6$ Hz, ortho C), 131.6 (s, para C), 130.2 (t, $J = 26$ Hz, ipso C), 129.2 (t, $J = 5$ Hz, meta C) (PPh_3)], 19.9 (d, $J(RhC) = 1.8$ Hz, 8-CH_3). IR (KBr): $\nu(CO)$ 1978 (s br) cm^{-1}. Λ_M (10^{-4} M in CH_2Cl_2) = 51.27 Ω^{-1} mol^{-1} cm^2.

[*trans*-Rh(CO)(mqH)($AsPh_3$)$_2$]BF_4 (5b). This compound was obtained in a quantitative yield by following a procedure similar to that reported for **5a** (reaction time 30 min). Anal. Calcd for $C_{47}H_{39}As_2BF_4NORh \cdot CH_2Cl_2$: C, 54.52; H, 3.91; N, 1.32. Found: C, 54.77; H, 3.80; N, 1.35. NMR (CD_2Cl_2): ^1H, δ 9.01 (dd, $J = 5.1$ Hz, $J = 1.4$ Hz, H-2), 7.87 (dd, $J = 8.2$ Hz, $J = 1.5$ Hz, H-4), 6.87 (dd, $J = 8.2$ Hz, $J = 5.1$ Hz, H-3), 3.50 (s, 8-CH_3); ^{13}C (CD_2Cl_2) δ 188.0 (d, $J(RhC) = 66$ Hz, Rh–CO), [152.2, 145.8, 140.5, 134.5, 132.1, 130.9, 128.9, 127.8, 120.9, 9 aromatic C, mqH], [133.2 (ortho C), 131.7 (ipso C), 131.3 (para C), 129.7 (meta C) ($AsPh_3$)], 19.9 (d, $J(RhC) = 2.0$ Hz, 8-CH_3). IR (KBr): $\nu(CO)$ 1976 (s br) cm^{-1}. Λ_M (10^{-4} M in CH_2Cl_2) = 52.31 Ω^{-1} mol^{-1} cm^2.

X-ray Structure Determination and Refinement. Crystals of [*trans*-Rh(CO)(mqH)(PPh_3)$_2$]$BF_4 \cdot 2.5CHCl_3$ were obtained from a chloroform solution of **5a**. Diffraction data were collected on a Siemens R3m/v four-circle diffractometer with an ω–2θ scan method using graphite-monochromated Mo Kα radiation. Unit-cell dimensions were determined from a least-squares fit of 30 reflections with $16° \leq \theta \leq 29°$. Two standards measured every 148 reflections showed no significant change.

The usual corrections for Lorentz and polarization effects were applied to the intensity data. Absorption corrections were not considered necessary. The positions of the Rh and P atoms were determined from a Patterson map. Other atoms were located from successive difference Fourier map calculations. The structure was refined by full-matrix least-squares methods. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms, from a ΔF map, were included with fixed coordinates and isotropic thermal parameters ($U = 0.08$ Å^2). The chloroform molecules were found during the refinement. One of the three solvent molecules lies near a center of symmetry and is only partially present. Its carbon (C(50)) and chlorine (Cl(7), Cl(8), and Cl(9)) atoms were assigned an occupancy of 0.5 and isotropic thermal parameters. The remaining solvent molecules were found in the general positions. However, the chlorine atoms of one of these molecules were disordered in two sets, A and B, with group occupancies of 0.48 and 0.52, respectively. The largest residual peak in the final difference map was 0.67 e Å^{-3} in height, in the vicinity of the Cl(8) atom. All calculations were performed by using the SHELXTL PLUS[21] and the PARST[22] computer programs.

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Supplementary Material Available: A figure giving an ORTEP diagram of **5a** and full tables of crystallographic and data collection parameters, bond distances and angles, anisotropic temperature factors, and hydrogen coordinates (7 pages). Ordering information is given on any current masthead page.

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