Table II. Final Positional and Anisotropic Thermal Parameters[a] (with Esd's)[b] for the Nonhydrogen Atoms of $(\eta^3\text{-}CH_2C_6H_5)Co[P(OCH_3)_3]_3$

atom	*x*	*y*	*z*	*B*(1,1)	*B*(2,2)	*B*(3,3)	*B*(1,2)	*B*(1,3)	*B*(2,3)
Co	0.24684 (4)	0.22518 (5)	0.11403 (2)	3.00 (2)	2.60 (2)	2.72 (2)	−0.12 (2)	0.26 (2)	0.08 (2)
P_1	0.30474 (9)	0.3617 (1)	0.17957 (4)	3.83 (4)	3.00 (4)	2.83 (4)	0.01 (4)	0.20 (3)	0.07 (4)
P_2	0.26677 (9)	0.3966 (1)	0.05538 (4)	3.42 (4)	3.10 (4)	3.17 (4)	0.19 (4)	0.46 (3)	0.52 (4)
P_3	0.07092 (9)	0.1579 (1)	0.13927 (4)	2.95 (4)	4.14 (5)	3.79 (4)	−0.03 (4)	0.34 (3)	0.33 (4)
O_{11}	0.4496 (2)	0.3774 (3)	0.19651 (9)	4.2 (1)	5.8 (2)	3.6 (1)	−0.8 (1)	−0.2 (1)	−0.6 (1)
O_{12}	0.2566 (3)	0.5352 (3)	0.17717 (10)	6.5 (1)	2.9 (1)	3.9 (1)	0.3 (1)	0.1 (1)	−0.2 (1)
O_{13}	0.2602 (2)	0.3231 (3)	0.23768 (9)	5.8 (1)	3.7 (1)	2.9 (1)	0.4 (1)	0.7 (1)	0.3 (1)
O_{31}	0.0072 (2)	0.2192 (4)	0.19166 (11)	4.4 (1)	6.6 (2)	4.8 (1)	0.8 (1)	1.2 (1)	−0.0 (1)
O_{32}	−0.0511 (2)	0.1824 (4)	0.10152 (11)	3.3 (1)	9.1 (2)	5.2 (1)	−0.2 (1)	−0.3 (1)	0.7 (2)
O_{33}	0.0616 (2)	−0.0231 (3)	0.15307 (11)	3.9 (1)	4.2 (1)	7.4 (2)	−1.0 (1)	1.5 (1)	1.2 (1)
O_{21}	0.1519 (2)	0.5058 (3)	0.03722 (10)	3.9 (1)	6.2 (2)	5.0 (1)	1.5 (1)	0.5 (1)	2.2 (1)
O_{22}	0.2932 (3)	0.3343 (4)	−0.00212 (10)	10.6 (2)	5.1 (1)	3.3 (1)	1.2 (2)	2.2 (1)	0.8 (1)
O_{23}	0.3742 (2)	0.5206 (3)	0.06539 (11)	4.4 (1)	3.9 (1)	7.2 (2)	−1.1 (1)	−0.5 (1)	2.4 (1)
C_{11}	0.5422 (4)	0.4038 (6)	0.1594 (2)	4.1 (2)	6.8 (3)	4.7 (2)	−1.5 (2)	0.2 (2)	−1.0 (2)
C_{12}	0.2814 (5)	0.6428 (5)	0.2193 (2)	11.0 (3)	3.4 (2)	5.4 (2)	0.1 (2)	0.5 (2)	−1.1 (2)
C_{13}	0.2846 (4)	0.1783 (5)	0.2609 (2)	7.6 (3)	4.8 (2)	3.9 (2)	1.0 (2)	0.8 (2)	1.3 (2)
C_{31}	−0.0442 (5)	0.3669 (6)	0.1948 (2)	7.6 (3)	6.7 (3)	7.5 (3)	1.5 (2)	2.6 (2)	−0.3 (3)
C_{32}	−0.0524 (4)	0.1788 (7)	0.0465 (2)	5.1 (2)	9.3 (3)	4.6 (2)	−0.2 (2)	−1.0 (2)	0.0 (2)
C_{33}	−0.0531 (4)	−0.0997 (6)	0.1621 (2)	5.9 (2)	6.6 (3)	9.3 (3)	−2.4 (2)	2.9 (2)	0.7 (3)
C_{21}	0.0765 (4)	0.5808 (6)	0.0731 (2)	5.7 (2)	6.7 (3)	6.1 (2)	2.9 (2)	1.0 (2)	1.4 (2)
C_{22}	0.2816 (5)	0.4100 (8)	−0.0502 (2)	7.6 (3)	13.5 (4)	4.0 (2)	2.0 (3)	0.6 (2)	1.5 (3)
C_{23}	0.3862 (5)	0.6668 (6)	0.0437 (2)	5.9 (2)	4.0 (2)	12.0 (4)	−0.4 (2)	0.3 (3)	2.4 (3)
C_1	0.2368 (4)	0.0527 (5)	0.0600 (1)	4.4 (2)	3.9 (2)	3.4 (2)	0.4 (2)	0.4 (1)	−0.4 (2)
C_2	0.3571 (3)	0.0434 (4)	0.0861 (1)	4.0 (2)	2.5 (2)	3.3 (2)	0.2 (1)	0.7 (1)	−0.5 (1)
C_3	0.3634 (4)	−0.0015 (5)	0.1390 (1)	4.2 (2)	3.7 (2)	4.1 (2)	0.8 (2)	0.7 (1)	0.2 (2)
C_4	0.4799 (4)	−0.0134 (5)	0.1659 (2)	5.5 (2)	5.5 (2)	4.2 (2)	1.5 (2)	−0.1 (2)	0.4 (2)
C_5	0.5857 (4)	0.0149 (6)	0.1410 (2)	3.7 (2)	6.7 (3)	6.3 (2)	1.5 (2)	−0.3 (2)	−0.7 (2)
C_6	0.5808 (4)	0.0645 (5)	0.0887 (2)	3.7 (2)	5.8 (2)	6.3 (2)	0.5 (2)	1.8 (2)	−0.9 (2)
C_7	0.4692 (4)	0.0812 (5)	0.0627 (1)	4.9 (2)	3.5 (2)	4.0 (2)	0.6 (2)	1.2 (2)	−0.4 (2)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(B(1,1)h^2a^{*2} + B(2,2)k^2b^{*2} + B(3,3)l^2c^{*2} + 2B(1,2)hka^*b^* + 2B(1,3)hla^*c^* + 2B(2,3)klb^*c^*)/4]$. [b] Numbers in parentheses are the estimated standard deviations and refer to the last significant digit of the preceding number.

Table III. Interatomic Distances (Å) and Angles (Deg) (with Esd's) for $(\eta^3\text{-}CH_2C_6H_5)Co[P(OCH_3)_3]_3$

	Distances		
Co–P_1	2.123 (1)	C_5–C_6	1.401 (5)
Co–P_2	2.129 (1)	C_6–C_7	1.357 (4)
Co–P_3	2.111 (1)	C_2–C_7	1.409 (4)
Co–C_1	2.036 (3)	P_1–O_{11}	1.609 (2)
Co–C_2	2.117 (3)	P_1–O_{12}	1.595 (2)
Co–C_3	2.408 (3)	P_1–O_{13}	1.613 (2)
C_1–C_2	1.435 (4)	O_{11}–C_{11}	1.423 (4)
C_2–C_3	1.404 (4)	O_{12}–C_{12}	1.442 (4)
C_3–C_4	1.409 (4)	O_{13}–C_{13}	1.410 (4)
C_4–C_5	1.352 (5)		
	Angles		
C_1–Co–C_2	40.36 (11)	C_1–C_2–C_3	117.97 (27)
C_1–Co–C_3	65.77 (11)	C_1–C_2–C_7	124.34 (28)
C_1–Co–P_1	161.85 (9)	C_2–C_3–C_4	119.68 (28)
C_1–Co–P_2	92.44 (9)	C_3–C_4–C_5	120.71 (31)
C_1–Co–P_3	88.87 (9)	C_4–C_5–C_6	120.27 (31)
C_2–Co–C_3	35.41 (10)	C_5–C_6–C_7	119.75 (31)
C_2–Co–P_1	122.07 (8)	C_6–C_7–C_2	121.76 (30)
C_2–Co–P_2	102.14 (8)	C_7–C_2–C_3	117.65 (27)
C_2–Co–P_3	114.86 (8)	Co–P_1–O_{11}	120.62 (9)
C_3–Co–P_1	96.63 (8)	Co–P_1–O_{12}	114.40 (8)
C_3–Co–P_2	133.72 (8)	Co–P_1–O_{13}	121.28 (9)
C_3–Co–P_3	99.13 (8)	P_1–O_{11}–C_{11}	122.35 (18)
P_1–Co–P_2	97.37 (3)	P_1–O_{12}–C_{12}	122.29 (21)
P_1–Co–P_3	98.77 (3)	P_1–O_{13}–C_{13}	120.96 (19)
P_2–Co–P_3	121.78 (3)		

There is a C–C bond length alternation in the benzyl ring of $(\eta^3\text{-}CH_2C_6H_5)Co[P(OCH_3)_3]_3$ (see Table III), which suggests that the η^3 coordination of the benzyl ligand results in some degree of localization in the π-electron structure of the ring. Similar phenomena have been observed in other π-benzyl structures.[3h,i,8,9]

Finally, we note that the coordination geometry of this pseudo-trigonal-bipyramidal structure is significantly different from that of the isoelectronic $(\eta^3\text{-cyclooctenyl})Co[P(OCH_3)_3]_3$ complex which better approximates a square pyramid.[10]

Acknowledgment. This structure determination was carried out as part of the University of California at Berkeley Chemistry Department's course entitled "Structure Analysis by Single Crystal X-ray Diffraction". We wish to thank our instructors, Professor K. N. Raymond, Professor S.-H. Kim, Mr. Bruce Gilbert, and Dr. Fred Hollander. Helpful discussions with Earl Muetterties are also acknowledged.

Registry No. $(\eta^3\text{-}CH_2C_6H_5)Co[P(OCH_3)_3]_3$, 51266-18-3.

Supplementary Material Available: Listing of observed and calculated structure factor amplitudes (11 pages). Ordering information is given on any current masthead page.

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(10) Tau, K. D.; Muetterties, E. L.; Day, V. W., private communication.

Contribution from the 3M Central Research Laboratories,
St. Paul, Minnesota 55101

Diketonate-Exchange Reactions of Palladium Bis(hexafluoroacetylacetonate)

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Previous research from this laboratory has outlined the extensive acid–base chemistry of palladium bis(hexafluoroacetylacetonate), $Pd(F_6acac)_2$.[1] The reactions of this fluorinated β-diketonate with organometallic compounds have been examined, and this paper reports those with rhodium and ruthenium hydrides. Metal hydrides were of interest because

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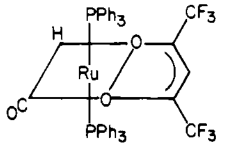
(1) A. R. Siedle and L. H. Pignolet, submitted for publication.

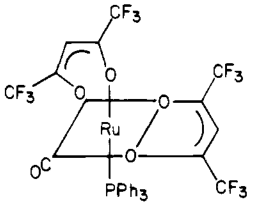
of the possibility that elimination of hexafluoroacetylacetone might lead to new polymetallic compounds. Instead, however, the chemistry observed involves an unusual exchange of hydride for hexafluoroacetylacetonate on rhodium and ruthenium.

Reactions between $MH_x(CO)_y(Ph_3P)_z$ and $Pd(F_6acac)_2$ were carried out in aromatic hydrocarbon solvents at 50–80 °C and the products separated from the resulting complex mixtures by preparative thin-layer chromatography. It appears that at least one carbonyl group is required to prevent complete reduction; $RuH_2(Ph_3P)_4$ and $(C_5H_5)_2ZrHCl$ gave metallic palladium in high yield.

Exemplary is $RuH_2(CO)(PPh_3)_3$, in which successive replacement of hydride by hexafluoroacetylacetonate gave $Ru(F_6acac)H(CO)(Ph_3P)_2$ (**1**) and $Ru(F_6acac)_2(CO)(Ph_3P)$ (**2**).



1



2

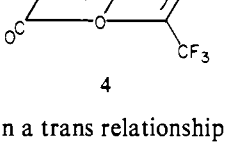
The proposed stereochemistry of these new six-coordinate 18-electron Ru(II) compounds is shown below and was inferred from the NMR spectroscopic data.

For **1**, the observation of two singlets in the ^{19}F NMR spectrum indicates that the two ends of the hexafluoroacetylacetonate ligand are nonequivalent which in turn requires that the hydride and carbonyl groups be trans to the ligating F_6acac oxygens. The two bulky triphenylphosphine groups may then be placed in the sterically unencumbered trans axial positions. This results in equivalent phosphine groups which is confirmed by the singlet in the $\{^1H\}^{31}P$ NMR spectrum and the 1:2:1 triplet for the Ru–H protons. The two-bond H–Ru–P coupling constant is 19 Hz, which is reasonable for hydride cis to phosphorus and compares favorably with the 20 Hz found in *trans*-$\{RuH(CO)[(C_2H_5)_2PC_2H_4P(C_2H_5)_2]_2\}BPh_4$.[2]

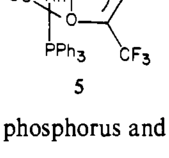
The ^{19}F NMR spectrum of **2** revealed four nonequivalent CF_3 groups, and the ^1H NMR spectrum shows that the F_6acac methine protons are also nonequivalent. This requires that the four oxygen termini of the hexafluoroacetylacetonate groups all be trans to different groups. Such an arrangement is consistent with a stereochemistry in which the hexafluoroacetylacetonate groups all are in different chemical environments and in which the triphenylphosphine and carbonyl groups are cis to one another as shown.

The hydride displacement reaction of $RuHCl(CO)(Ph_3P)_3$ produced $Ru(F_6acac)Cl(CO)(Ph_3P)_2$ (**3**). Its ^{19}F NMR spectrum displayed two singlets and the $\{^1H\}^{31}P$ spectrum comprised a singlet, indicating that the structure of **3** is analogous to that of **1** with hydride replaced by chloride.

From $RhH(CO)(Ph_3P)_3$ and $Pd(F_6acac)_2$ was obtained the four-coordinate Rh(I) complex $Rh(F_6acac)(CO)(Ph_3P)$ (**4**). In **4**, the two CF_3 groups are required to be nonequivalent, one being in a trans relationship to phosphorus and the other to the carbonyl group, and, indeed, two singlets are observed in the ^{19}F spectrum. The $\{^1H\}^{31}P$ NMR spectrum is the expected doublet with $J_{Rh-P} = 175$ Hz.



4



5

From the reaction of hexafluoroacetylacetone and $RhH(CO)(Ph_3P)_3$ was obtained a 16% yield of $Rh(F_6acac)(CO)(Ph_3P)_2$ (**5**) and no **4**. The ^{19}F NMR spectrum of this compound contained only one sharp singlet, and the $\{^1H\}^{31}P$ NMR spectrum comprised a broad ($W/2 = 90$ Hz) singlet. It is probable that **5** contains trigonal-bipyramidal Rh(I) with a symmetrical bidentate hexafluoroacetylacetonate ligand occupying two of the equatorial positions; placement of the two triphenylphosphine groups in trans axial positions is reasonable on steric grounds.

Phosphine carbonyl hydrides of rhodium and ruthenium undergo replacement of hydride by hexafluoroacetylacetonate when treated with palladium bis(hexafluoroacetylacetonate), a reaction apparently not reported for other covalent metal β-diketonates. Indeed, while hydride replacement also occurs with $RuHCl(CO)(Ph_3P)_3$, chloride and not hydride is displaced by triethylammonium hexafluoroacetylacetonate.[3] In the resulting rhodium and ruthenium hexafluoroacetylacetonates, the β-diketonate acts as a bidentate, oxygen-bonded ligand, and there are displaced a sufficient number of triphenylphosphines to achieve this bonding mode. In contrast, triphenylphosphine forms with $Pd(F_6acac)_2$ in nonpolar solvents $Pd(F_6acac)_2PPh_3$ which contains one bidentate and one monodentate oxygen-bonded F_6acac ligand. The yields in the replacement reactions reported here are low for several reasons: there is a competing reduction of $Pd(F_6acac)_2$ to palladium metal, and the triphenylphosphine released converts $Pd(F_6acac)_2$ to the less reactive $Pd(F_6acac)_2PPh_3$. Better yields, as in the case of **1** and **3**, have been obtained by Queiros and Robinson[3] from the reaction of $RuHCl(CO)(Ph_3P)_3$ or, inter alia, $RuH_2(CO)(Ph_3P)_3$ with hexafluoroacetylacetone.

Experimental Section

Rhodium and ruthenium compounds were prepared by the methods described by Robinson and Uttley[4] and reactions involving them were carried out under nitrogen. NMR spectra were obtained on a Varian XL-100 spectrometer and infrared spectra on an instrument with grating optics.

$Ru(F_6acac)H(CO)(Ph_3P)_2$ and $Ru(F_6acac)_2(CO)(Ph_3P)$. A mixture of 0.65 g (0.7 mmol) of $RuH_2(CO)(Ph_3P)_3$ and 0.37 g (0.7 mmol) of $Pd(F_6acac)_2$ in 25 mL of benzene was refluxed and stirred for 16 h. The reaction mixture was chromatographed on a 12 × 1 in. silica gel column; elution with benzene gave a crude product. This was subjected to thin-layer chromatography on silica gel. Hexane was used to elute 0.03 g of yellow $Ru(F_6acac)_2(CO)(Ph_3P)$, mp 181–184 °C, after recrystallization from hexane. Continued development of the TLC plate with 1:1 hexane–benzene afforded 0.05 g of $(Ph_3P)_2RuH(CO)(F_6acac)$, mp 128–129 °C, after recrystallization from hexane.

$Ru(F_6acac)H(CO)(Ph_3P)_2$ (1). Anal. Calcd: C, 58.5; H, 3.7. Found: C, 58.5; H, 3.7. IR (KBr): 3060 (w), 1950 (s, Ru–H), 1935 (s, Ru–CO), 1630 (s), 1545 (w), 1480 (m), 1435 (s), 1255 (s), 1210 (s), 1145 (s), 1090 (m), 740 (m), 690 (s), 515 (s) cm^{-1}. ^1H NMR ($CDCl_3$): −14.5 (t, $J_{P-H} = 19$), 4.68 ppm. ^{19}F NMR ($CDCl_3$): 75.25, 76.46 ppm. ^{31}P NMR ($CDCl_3$): 39.7 ppm.

$Ru(F_6acac)_2(CO)(Ph_3P)$ (2). Anal. Calcd: C, 43.0; H, 2.2. Found: C, 43.5; H, 2.1. IR (KBr): 3060 (w), 1990 (s, Ru–CO), 1625 (s), 1600 (m), 1555 (m), 1480 (m), 1465 (s), 1435 (m), 1345 (m), 1265 (s), 1210 (s), 1155 (s), 1100 (m), 800 (m), 745 (m), 690 (s), 350 (m) cm^{-1}. ^1H NMR ($CDCl_3$): 6.15, 5.74 ppm. ^{19}F NMR ($CDCl_3$): 74.92, 45.07, 75.63, 75.89 ppm. ^{31}P NMR ($CDCl_3$): 49.0 ppm.

$Ru(F_6acac)Cl(CO)(Ph_3P)_2$ (3). Palladium bis(hexafluoroacetylacetonate) (0.33 g (0.63 mmol)) and 0.60 g (0.63 mmol) of $RuHCl(CO)(Ph_3P)_3$ in 12 mL of toluene were heated overnight at

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(2) G. M. Bancroft, M. J. Mays, B. E. Prater, and F. P. Stefanini, *J. Chem. Soc. A*, 2146 (1970).

(3) M. A. M. Queiros and S. D. Robinson, *Inorg. Chem.*, **17**, 310 (1978).

(4) N. Ahmad, J. J. Levison, S. D. Robinson, and M. F. Uttley, *Inorg. Synth.*, **15**, 45 (1974).

60 °C. Chromatography on a 12 × 1 in. silica gel column have a crude yellow product which was purified by preparative thin-layer chromatography. Benzene–hexane (1:1) developed a yellow band which yielded 0.03 g of a semicrystalline yellow material, which was not successfully purified, and an orange band. The latter was rechromatographed with use of pure benzene to give 0.1 g (18%) of the desired product as orange crystals, mp 202–205 °C. Anal. Calcd: C, 56.3; H, 3.5; Cl, 3.9. Found: C, 56.5; H, 3.5; Cl, 4.4. IR (KBr): 3060 (w), 1962 (s, Ru–CO), 1620 (s), 1545 (w), 1485 (m), 1475 (s), 1440 (s), 1260 (s), 1210 (s), 1155 (s), 1145 (s), 1095 (m), 785 (w), 745 (m), 690 (s), 515 (s), 320 (m, RuCl) cm^{-1}. ^1H NMR ($CDCl_3$): 4.87 ppm. ^{19}F NMR ($CDCl_3$): 74.31, 74.76 ppm. ^{31}P NMR ($CDCl_3$): 27.4 ppm. Electronic spectrum ($CHCl_3$) [λ_{max} (log ϵ)]: 239 (4.44), 260 (4.38), 280 (sh) nm.

$Rh(F_6acac)(CO)(Ph_3P)$ (4). A solution of 0.46 g (0.5 mmol) of $Rh(CO)H(Ph_3P)_3$ and 0.26 g (0.5 mmol) of $Pd(F_6acac)_2$ in 20 mL of toluene was heated for 12 h at 50 °C and then chromatographed on a silica gel column as before. Dichloromethane eluted a yellow compound which was further purified by preparative TLC (silica, benzene). Recrystallization from acetone–ethanol gave 0.065 g (22%) of the product as orange flakes, mp 164–165.5 °C. Anal. Calcd: C, 48.0; H, 2.7. Found: C, 47.8; H, 2.6. IR (KBr): 3060 (w), 1999 (s, Rh–CO), 1630 (m), 1610 (s), 1560 (w), 1530 (w), 1460 (s), 1490 (m), 1485 (m), 1260 (s), 1200 (m), 1150 (s), 1100 (s), 805 (s), 750 (s), 745 (sh), 690 (s), 675 (m), 580 (m), 535 (m), 535 (m), 525 (m), 505 (m) cm^{-1}. ^1H NMR ($CDCl_3$): 6.24 ppm. ^{19}F NMR ($CDCl_3$): 75.52, 75.71 ppm. ^{31}P NMR ($CDCl_3$): 47.7 ppm (J_{Rh-P} = 178). Electronic spectrum ($CHCl_3$) [λ_{max} (log ϵ)]: 240 (4.29), 264 (3.98), 270 (3.98), 325 (3.90) nm.

$Rh(F_6acac)(CO)(Ph_3P)_2$ (5). A mixture of 0.20 g (0.22 mmol) of $RhH(CO)(Ph_3P)_3$ and 0.05 g (0.22 mmol) of hexafluoroacetylacetone in 10 mL of toluene was heated for 30 min at 80 °C and then evaporated onto 5 g of silica gel. This was placed atop a 6 × $^1/_2$ in. column made up in hexane. Benzene–hexane (1:1) eluted a trace of unidentified orange material. Pure benzene eluted $(Ph_3P)_2Rh(CO)(F_6acac)$, 0.03 g (16%), as yellow needles, mp 147–148 °C, after recrystallization from ethanol. Anal. Calcd: C, 58.5; H, 3.6. Found: C, 58.8; H, 3.6. IR (KBr): 3060 (w), 1980 (s, Rh–CO), 1670 (s), 1535 (m), 1520 (m), 1480 (w), 1440 (s), 1255 (s), 1200 (s), 1140 (s), 1095 (s), 785 (w), 740 (m), 690 (s), 660 (m), 520 (s), 505 (s) cm^{-1}. ^1H NMR ($CDCl_3$): 4.66 ppm. ^{19}F NMR ($CDCl_3$): 76.0 ppm. ^{31}P NMR ($CDCl_3$): 29.0 ($W/2$ = 90) ppm.

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Registry No. 1, 64567-30-2; **2**, 76136-84-0; **3**, 64567-27-7; **4**, 76136-85-1; **5**, 76189-27-0; $Pd(F_6acac)_2$, 64916-48-9; $RuH_2(CO)(Ph_3P)_3$, 25360-32-1; $RuHCl(CO)(Ph_3P)_3$, 16971-33-8; $Rh(CO)H(Ph_3P)_3$, 17185-29-4.

Contribution from Union Carbide Corporation,
Technical Center, Tarrytown, New York 10591

Migration and Localization of Thallium in Zeolites following Ozonation

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The redox behavior and localization of metal ions and metal-containing phases in ion-exchanged zeolites have been extensively studied[1–4] because of their potential impact on the performance and regenerability of metal-exchanged zeolite catalysts. For example, it was reported[2,5,6] that treatment of Pd^{2+}–Y, Cu^{2+}–Y, and Ag^+–Y zeolites with hydrogen at high temperatures caused formation of metal crystallites on the surface of the zeolites or of metal agglomerates in the pores. In some cases, high-temperature oxidation with oxygen reoxidized the metal particles to ions (rather than metal oxides), which then migrated back into the zeolite matrix.[7,8] However, oxide phases dispersed between zeolite crystals have also been identified.[7–9] In a study of the regeneration and reuse of immobilized thallium reagents as organic oxidants, we have observed the room-temperature migration of thallium from internal sites to the surface when Tl^+-exchanged zeolites were oxidized with moist ozone. On reduction, the ions returned to sites within the zeolite structure. However, the redox bulk ⇄ surface migration is only partially reversible.

This partial reversibility[3,7] and the need for hydration[10] have been reported by others studying redox migration of ions in zeolite. Otherwise, our results differ from most previously published studies on the subject. Notably, thallium migration occurred at 23–25 °C as opposed to the 100–400 °C range required to effect migration of Ag, Cu, Ni, Pt, and Pd. Additionally, the direction of thallium migration is the reverse of that usually observed with other metals.

All the data reported herein were obtained on a Linde proprietary synthetic zeolite[11] (referred to here as Zeo) with $SiO_2/Al_2O_3 = 49$, which was ion exchanged with Tl^+. However, qualitatively similar observations were also made with Tl^+–Y and Tl^+–mordenite. It is known that the Linde zeolite has a 6-Å pore size, but other details of the structure are yet to be determined.

Three successive treatments of H^+–Zeo with aqueous $TlNO_3$ under reflux produced Tl^+–Zeo (A) having an atom ratio of $Tl/Al = 0.93 \pm 0.14$. NO_3^- analysis of A confirmed the absence of $TlNO_3$ contamination. Exposure of A to moist ozone (2 wt % in O_2) at 23–25 °C and 0.5 L min^{-1} for 2–8 h caused the white solid to change to a dark brown material (B). The requirement for water as a coreactant was established by ozonation of A, which was previously dried at 108 °C in vacuo for 11 h, under rigorously anhydrous conditions. No color change occurred, and HF dissolution of the white powder followed by iodometric titration demonstrated the total absence of Tl(III).

One could envision two simple reactions by which Tl(III) could be formed in the zeolite pores to balance the framework anionic charge (designated Zeo^-), viz., eq 1 and 2. [Zeo is

$$\mathrm{Tl^+{-}Zeo^- + O_3 \rightarrow (TlO)^+Zeo^- + O_2} \qquad (1)$$

$$\mathrm{Tl^+{-}Zeo^- + O_3 + H_2O \rightarrow Tl(OH)_2{}^+Zeo^- + O_2} \qquad (2)$$

used as a convenient abbreviation. It is not intended as a new nomenclature and it is not the Union Carbide name for the zeolite.] Instead, we found that the thallium ions migrate to form brown Tl_2O_3 on the surface of the zeolite particles (eq 3). The framework charge neutrality is presumably main-

$$\mathrm{2(Tl^+{-}Zeo^-) + 2O_3 + H_2O \rightarrow 2(H^+{-}Zeo^-) + 2O_2 + Tl_2O_3} \qquad (3)$$

tained by protons from water vapor, while the driving force for migration arises, at least in part, from the energy of crystallization of Tl_2O_3.

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(1) P. Jacobs, M. Tielen, J. P. Linart, J. B. Uytterhoeven, and H. Beyer, *J. Chem. Soc., Faraday Trans. 1*, **72**, 2793 (1976).
(2) H. Beyer, P. Jacobs, and J. B. Uytterhoeven, *J. Chem. Soc., Faraday Trans. 1*, **72**, 674 (1976).
(3) P. Jacobs, J. B. Uytterhoeven, and H. Beyer, *J. Chem. Soc., Faraday Trans. 1*, **73**, 1755 (1977).
(4) P. A. Jacobs, J. P. Linart, H. Nijs, J. B. Uytterhoeven, and H. Beyer, *J. Chem. Soc., Faraday Trans. 1*, **73**, 1745 (1977).
(5) M. Primet and Y. B. Tarit, *J. Phys. Chem.*, **81**, 1317 (1977).
(6) P. Gallezot and B. Imelik, *Adv. Chem. Ser.*, No. **121**, 66 (1973).
(7) R. G. Herman, J. H. Lunsford, H. Beyer, P. Jacobs, and J. Uytterhoeven, *J. Phys. Chem.*, **79**, 2388 (1975).
(8) A. A. Slinkin, G. V. Antoshin, M. Loktev, E. Shapiro, et al., *Kinet.* Catal. (Engl. Transl.), **19** (3), 595 (1978).
(9) Magee and Blazek *ACS Monogr.*, No. **171**, 655–656 (1976).
(10) G. Jones and M. Davies, *J. Chem. Soc., Faraday Trans. 1*, **71**, 1791 (1975).
(11) R. W. Grose and E. M. Flanigen, *Ger. Offen.*, **GER. OFFEN. 2,704,039** (Aug 18, 1977).

0020-1669/81/1320-1320$01.25/0