thermostated to ±1 °C. The amount of CH_4 evolved at time *t* was calculated from a relative peak area of CH_4 to that of the reference by gas chromatography.

Spectral Measurement and Analysis. IR and NMR spectra were recorded on a Hitachi 295 spectrometer and JEOL PS-100 spectrometer, respectively. The analysis of gaseous and liquid products were carried out with a Shimadzu GC-3BT or GC-3BF gas chromatograph. Amounts of gases were measured by a Toepler pump. The microanalysis of carbon, hydrogen, and nitrogen was performed by Mr. T. Saito of our laboratory with a Yanagimoto CHN Autocorder Type MT-2.

Registry No. 1a, 32354-35-1; **1b,** 80976-38-1; **2,** 25360-32-1; **3,** 61817-37-6; $RhH(PPh_3)_4$, 18284-36-1; $RuH_2(PPh_3)_4$, 19529-00-1; $CH_3COOC_6H_5$, 122-79-2; CH_3COO-*p*-C_6H_4OMe, 1200-06-2; $C_2H_5COOC_6H_5$, 637-27-4; CH_3COO-*o*-C_6H_4OMe, 613-70-7; CH_3COO-*p*-C_6H_4CN, 13031-41-9; *n*-$C_4H_9COOC_6H_5$, 20115-23-5; *n*-$C_9H_{19}COOC_6H_5$, 14353-75-4; $C_6H_5COOC_6H_5$, 93-99-2; *n*-$C_3H_7COOC_2H_5$, 105-54-4; *n*-C_3H_7COO-*n*-C_4H_9, 109-21-7; C_2H_5COO-*n*-C_3H_7, 106-36-5.

Syntheses of Cationic and Zwitterionic Cyclobutadiene Compounds of Cobalt(I). Crystal and Molecular Structure of Tricarbonyl(η-1-methoxy-3-methyl-2-phenylcyclobutadiene)-cobalt(1+) Hexafluorophosphate

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The (η^3-cyclobutenonyl)cobalt complexes **1** react with trialkyloxonium salts to yield cationic cyclobutadiene compounds **2**, which have been characterized by IR, ^1H NMR, and ^{13}C NMR spectroscopy. Compounds **1** also react with $BF_3 \cdot OEt_2$ to afford the zwitterionic cyclobutadiene derivatives **4**. Reactions of **1b** with $PhCO^+SbF_6^-$ or $(CF_3SO_2)_2O$ produce **6** and **7**, respectively. The CO ligands in **2a** are displaced in refluxing benzene, affording the cationic sandwich complex **8**, and the unstable zwitterion **4g** can be trapped in refluxing benzene to give the zwitterionic sandwich complex **9**. An X-ray crystallography investigation of **2i** at −100 °C revealed a monoclinic crystal with space group $P2_1/c$ (No. 14): a = 14.689 (5) Å, b = 8.444 (2) A, c = 14.865 (5) Å, β = 109.32 (3)°, Z = 4, R = 0.087, R_w = 0.051. The cyclobutadiene ring is planar, and substituent atoms bound to the ring are displaced away from the metal. The carbon–carbon distances within the cyclobutadiene ring are unequal, as are the cobalt–carbon distances.

Introduction

Cyclobutadiene, the simplest cyclic polyene, has intrigued, chemists for decades. Its structural simplicity is deceptive, however, and this prototype antiaromatic molecule usually can only be isolated at low temperatures in a noble-gas matrix,[2] unless equipped with highly bulky substituents.[3] While the square D_{4h} geometry of cyclobutadiene is predicted to be a triplet diradical ground state, theoretical studies agree in predicting that the molecule will distort to a D_{2h} rectangular singlet;[4] spectroscopic[5] and chemical[6] evidence has also been presented to this effect.

Since the original prediction that cyclobutadiene should be stabilized by interaction with a transition-metal center,[7] the organometallic chemistry of this ligand has been explored extensively.[8] There are two methods generally available for the synthesis of a coordinated cyclobutadiene ligand. The first involves the use of a preformed four-membered ring in the form of 3,4-dihalocyclobutenes,[9,10] 1,2,3,4-tetrahalocyclobutanes,[11] or photo α-pyrones,[12] while the second forms the cyclobutadiene within the coordination sphere of the metal by the cyclodimerization of two alkynes.[13–15] We have described a convenient synthesis

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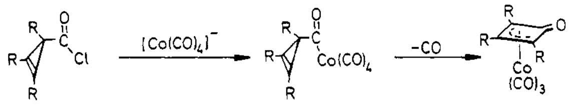
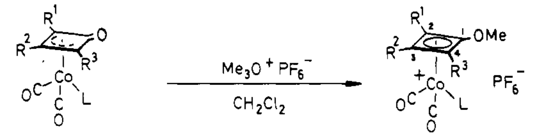
of a variety of substituted (η^3-cyclobutenonyl)cobalt compounds by the ring expansion of (2-cyclopropene-1-carbonyl)cobalt compounds;[16,17] this method is particularly versatile in the number of different substituent patterns which can be incorporated with ease into the acyl chloride precursor.[17]



This paper describes nucleophilic reactions of the ketonic oxygen atom of the cyclobutenonyl ring which lead to cobalt compounds containing coordinated cyclobutadiene ligands. Some results have been the subject of a preliminary communication.[18]

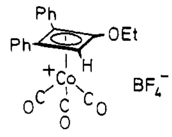
Results and Discussion

The η^3-cyclobutenonyl compounds **1** were quantitatively transformed into the cationic η^4-cyclobutadiene complexes **2** or **3** by treatment with 1 M equivalent of a trialkyloxonium salt in CH_2Cl_2 solution at room temperature. The reaction was usually complete within 4 h, as evidenced by IR monitoring, and the products **2** or **3** could be obtained as crystalline, yellow materials after evaporation and recrystallization.



1. 2.

a, $R^1 = R^2 = Ph$, $R^3 = H$, L = CO; b, $R^1 = R^2 = Ph$, $R^3 = H$, L = PPh_3; c, $R^1 = R^2 = Ph$, $R^3 = H$, L = PPh_2Me; d, $R^1 = R^2 = Ph$, $R^3 = H$, L = $PPhMe_2$; e, $R^1 = R^2 = Ph$, $R^3 = H$, L = PEt_3; f, $R^1 = R^2 = Et$, $R^3 = H$, L = CO; g, $R^1 = R^2 = Et$, $R^3 = H$, L = PPh_3; h, $R^1 = Me$, $R^2 = Ph$, $R^3 = H$, L = CO; i, $R^1 = Ph$, $R^2 = Me$, $R^3 = H$, L = CO; j, $R^1 = Ph$, $R^2 = Me$, $R^3 = H$, L = PPh_3; k, $R^1 = Ph$, $R^2 = H$, $R^3 = Me$, L = CO; l, R^1 = *t*-Bu, $R^2 = R^3 = H$, L = CO; m, R^1 = *t*-Bu, $R^2 = R^3 = H$, L = PPh_3; n, $R^1 = R^3 = H$, R^2 = *t*-Bu, L = $PPhMe_2$; o, R^1 = *n*-Bu, $R^2 = R^3 = H$, L = CO



3.

As expected, the metal carbonyl stretching bands for cationic compounds **2** appear at higher frequency than do those of their precursors **1**.[17] The tricarbonyl compounds exhibit only two ν_{CO} bands (A_1 + E) in CH_2Cl_2, characteristic of local C_{3v} symmetry. ^1H NMR resonances for the ring protons of **2** (Table I) appear in the range δ 5.0–7.0; this represents significant deshielding of these protons compared to chemical shifts in neutral η^4-cyclobutadiene compounds (δ 3.5–5.5)[8] but is quite compatible with the observed chemical shift (δ 6.14 in acetone) of the isoelectronic cationic complex $[Fe(\eta\text{-}C_4H_4)(CO)_2(NO)]^+PF_6^-$.[19] Similarly, phosphine-substituted compounds **2** generally exhibit spin–spin coupling of the ring protons to ^{31}P in the

Table I. ^1H NMR Data for Cationic Cyclobutadiene Compounds 2 and 3[a]

compd	δ^b OMe	R¹	R²	R³	other
2a	4.23 (s)	7.7–7.3 (m)		6.59 (s, $^3J_{^{13}C_1\text{-OMe}}$ = 5.0 Hz)	
2b	3.82 (s)	7.6–7.3 (m)		6.06 (d, J_{P-H} = 3.2)	7.6–7.3 (m, PPh_3)
2c	3.98 (s)	7.5–7.3 (m)		6.07 (d, J_{P-H} = 8.9)	2.15 (d, J_{P-H} = 8.9 PPh_2*Me*)
2d	4.01 (s)	7.5–7.2 (m)		5.97 (d, J_{P-H} = 5.2)	1.89 (d, J_{P-H} = 10.7, P*Me*) 1.71 (d, J_{P-H} = 11.9, P*Me*)
2e	4.04 (s)	7.7–7.3 (m)		6.06 (d, J_{P-H} = 4.9)	1.8–0.7 (m, P*Et*$_3$)
2f	4.03 (s)	2.4–2.0 (m), 1.11 (t), 1.27 (t)		6.05 (s)	
2g	3.55 (s)	2.2–1.5 (m), 1.21 (t), 0.98 (t)		5.31 (d, J_{P-H} = 2.6)	7.6–7.3 (m, PPh_3)
2h	4.12 (s)	2.27 (s)	7.42 (s)	6.64 (s)	
2i	4.21 (s)	7.53 (m)	2.27 (s)	6.33 (s)	
2j	3.75 (s)	7.7–7.3 (m)	1.64 (d, J_{P-H} = 2.4)	5.83 (d, J_{P-H} = 3.0)	7.7–7.3 (m, PPh_3)
2k	4.29 (s)	7.5–7.4 (m)	6.06 (s)	2.25 (s)	
2l[c]	4.08 (s)	1.30 (s)	6.20 (s)	5.73 (s)	
2m	3.94 (s)	1.33 (s)	5.31 (s)	5.24 (d, J_{P-H} = 4.5)	7.5 (m, PPh_3)
2n	3.30 (s)	. . .	1.05 (s)	5.02 (d, J_{P-H} = 0.7)	1.91 (d, J_{P-H} = 9.4, PPh*Me*$_2$)
2n[c]	3.59 (d, J_{P-H} = 0.5)	. . .	1.17 (s)	5.53 (d, J_{P-H} = 0.7)	2.14 (d, J_{P-H} = 9.4, PPh*Me*$_2$)
2o	4.00 (s)	2.18 (t, J_{H-H} = 7.5), 1.7–1.3 (m), 0.98 (t, J_{H-H} = 7.0)	5.72 (s)	5.38 (s)	
3	4.67 (m), 1.54 (t, J_{H-H} = 7.1)	7.7–7.3 (m)		6.93 (s)	

[a] For numbering see drawing in text. [b] In ppm downfield from internal Me_4Si, *J* in Hz; s = singlet, d = doublet, t = triplet, m = multiplet; measured at 60 MHz in $CDCl_3$ unless otherwise indicated. [c] Acetone-d_6, −90 °C.

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Table II. $^{13}C\{^1H\}$NMR Data for Compounds 2 and 3

	δ^a					
compd	C1	C2	C3	C4	OR	other
2a	146.0^c	87.4	81.5	65.6^d	62.1	132.5, 131.9, 128.9, 128.1, 127.7 (Ph); 198.3 (M-CO)
2b	143.9	79.3	65.8	65.3	62.3	131.1, 133.5 (Ph)
2f	148.8	95.7	91.3	68.4	62.2	19.23 (CH_2); 12.5 (CH_3)
2g	143.4	85.7	84.6	65.8	60.7	18.3 (CH_2); 12.7 (CH_3); 133.1, 132.3, 131.7, 131.6, 129.9, 129.8, 129.1 (Ph)
2h	148.4	*g*	*g*	*g*	62.2	11.4 (CH_3); 131.4, 130.3, 126.8 (Ph)
2n	139.3	60.3	94.7	60.3	61.4	30.4 (*C*CH_3); 29.6^e (CCH_3); 17.0^f (P-CH_3); 136.0, 131.0, 129.9, 129.6, 129.2, 128.9 (Ph)
3	146.6	87.8	82.3	66.7	73.8, 14.2	131.7, 131.4, 130.2, 129.4, 129.0, 127.3 (Ph)

^{a} For numbering, see drawing of 2 in text. In ppm downfield of internal Me_4Si. Measured at 15 MHz in acetone-d_6 unless otherwise stated. ^{b} $CDCl_3$ solution. ^{c} $^1J_{C4\text{-}C1} = 40.8 \pm 1.2$ Hz. ^{d} $^1J_{CH} = 201.6 \pm 1.2$ Hz. ^{e} $^1J_{PC} = 1.8$ Hz. ^{f} $^1J_{PC} = 31.1$ Hz. ^{g} Could not be observed.

Table III. ^1H NMR Data for Zwitterionic Cyclobutadiene Compounds 4

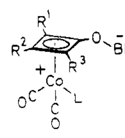
	δ^a		
compd	R^1	R^2	R^3
4a	2.13 (m, 2 H), 1.33 (t, $J_{H\text{-}H} = 7.3$ Hz, 3 H)	1.23 (d, qt, $J_{H\text{-}H} = 15.1, 7.2$ Hz, 1 H), 0.96 (d, qt, $J_{H\text{-}H} = 15.1, 7.2$ Hz, 1 H), 0.80 (t, $J = 7.2$ Hz, 3 H)	4.53 (d, qt, $J_{P\text{-}H} = 4.6$ Hz, $^5J_{F\text{-}H} = 1.6$ Hz, 1 H)
4b	6.8-8.0 (m, 25 H)		5.02 (d, qt, $J_{P\text{-}H} = 4.5$ Hz, $^5J_{F\text{-}H} = 1.8$ Hz, 1 H)
4c	7.6-7.2 (m, 20 H)	1.18 (s, 3 H)	4.67 (d, qt, $J_{P\text{-}H} = 4.4$ Hz, $^5J_{F\text{-}H} = 1.8$ Hz, 1 H)
4d	1.24 (s, 9 H)	3.75 (s, 1 H)	4.26 (d, qt, $J_{P\text{-}H} = 4.8$ Hz, $^5J_{F\text{-}H} = 1.6$ Hz, 1 H)
4e	2.07 (d, $J_{P\text{-}H} = 6.7$ Hz, 3 H)	6.8-7.8 (m, 20 H)	4.84 (d, qt, $J_{P\text{-}H} = 4.2$ Hz, $^5J_{F\text{-}H} = 1.4$ Hz, 1 H)
4f	7.2-7.2 (m, 20 H)	4.47 (s, 1 H)	1.55 (d, $J_{P\text{-}H} = 5.4$ Hz, 3 H)

^{a} In ppm downfield from internal Me_4Si; measured at 60 MHz in $CDCl_3$ solution (^{19}F NMR data in Experimental Section).

range 2.4–5.5 Hz; coupling of this magnitude has been observed for the cationic analogue $[Fe(\eta\text{-}C_4H_4)(CO)(NO)(PPh_3)]^+PF_6^-$ ($J_{PH} = 2.0$ Hz).[19] Compound **2n** is an exception, exhibiting only a 0.7-Hz coupling from ^{31}P to the ring proton; the reason for this is unclear, but anomalously small coupling has also been noted for its precursor **1n**.[17] Also compound **2m** only exhibits phosphorus coupling to the ring proton at position R^3, the proton at R^2 resonating as a singlet; once again similar phenomena have been noted for the precursor **1m**.[17] The methyl group in **2j** exhibits coupling to ^{31}P of 2.4 Hz, similar to that reported for $[Co(\eta\text{-}C_4Me_4)(I)(CO)(PPh_3)]$ (3.8 Hz).[20] As expected, compound **2d**, containing an unsymmetrically substituted cyclobutadiene ring, exhibits two ^1H NMR resonances due to the diastereotopic methyl groups on phosphorus, whereas **2n** shows only a single methyl resonance, even at −90 °C. This latter observation can be interpreted to mean that rotation about the metal to cyclobutadiene ring axis is still rapid on the ^1H NMR time scale at this temperature or that the molecular ground state is symmetrical, with the phosphorus atom occupying a site on the mirror plane.

^{13}C NMR data for compounds **2** and **3** are reported in Table II. Notably no coupling of ^{31}P to the cyclobutadiene ring carbon atoms was observed. The values of $^1J_{^{13}C\text{-}^{13}C}$ and $^1J_{^{13}C\text{-}^1H}$ for a ^{13}C-enriched sample of **2a** have been discussed in a separate paper.[21] More recently values of $^1J_{^{13}C\text{-}^{13}C}$ for neutral (cyclobutadiene)cobalt species $[Co(\eta\text{-}C_4R_4)(\eta\text{-}C_5H_5)]$ have been reported.[15] There is considerable disparity between the value of $J_{^{13}C\text{-}^{13}C}$ for cationic **2a** (40.8 ± 1.2 Hz) and the neutral compounds (24.1 Hz);[15] the reason for this difference remains to be explained, but it is notable that both values are significantly less than the corresponding one-bond couplings reported for 1,1′-dimethylferrocene (47 Hz)[22] and substituted arenes (54–70 Hz),[23] consistent with arguments which predict greater p character in the orbitals used to bond between carbon atoms in the ring as the ring size is decreased.[24]

The ketonic oxygen atom of compounds **1** also exhibits an affinity for other Lewis acids. Treatment of the appropriate complex **1** with $BF_3 \cdot OEt_2$ resulted in a rapid reaction to form the zwitterionic cyclobutadiene derivatives **4a–f**, which could be isolated as stable, crystalline compounds after evaporation of the solvent. Stable BF_3 adducts could not be isolated unless a triphenylphosphine ligand was present on the metal; the tricarbonyl com-



4.

a, $R^1 = R^2 = Et$, $R^3 = H$, L = PPh_3; b, $R^1 = R^2 = Ph$, $R^3 = H$, L = PPh_3; c, $R^1 = Ph$, $R^2 = Me$, $R^3 = H$, L = PPh_3; d, $R^1 = t\text{-Bu}$; $R^2 = R^3 = H$, L = PPh_3; e, $R^1 = Me$, $R^2 = Ph$, $R^3 = H$, L = PPh_3; f, $R^1 = Ph$, $R^2 = H$, $R^3 = Me$, L = PPh_3; g, $R^1 = R^2 = Ph$, $R^3 = H$, L = CO; h, $R^1 = R^2 = Et$, $R^3 = H$, L = CO

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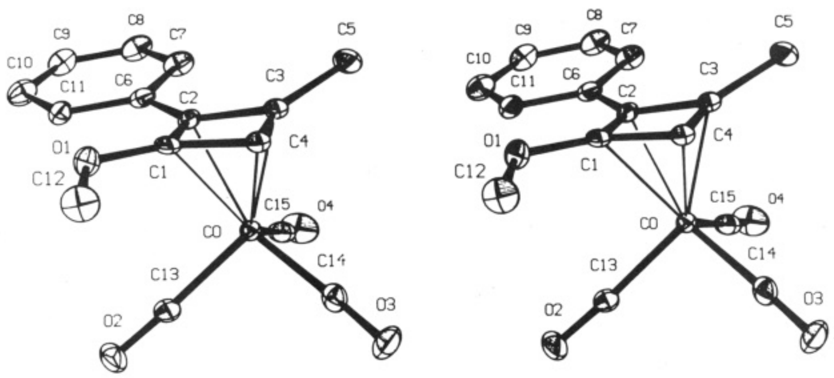
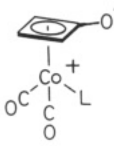


Figure 1. ORTEP stereoview of the cationic portion of **2i**, showing the atomic numbering scheme.

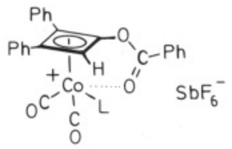
pounds **4g** and **4h** could be observed in solution by IR spectroscopy, but evaporation led only to recovery of the starting ketone. We have commented previously that substitution of a CO ligand in **1** by a tertiary phosphine causes a significant lowering of the C=O stretching frequency for the ring ketone; this was interpreted in terms of an increased contribution of canonical form **5** to the bonding in cyclobutenonyl complexes.[16] The increased Lewis basicity of the ketonic oxygen when L is changed from CO to PPh_3 would seem to substantiate this idea.



5.

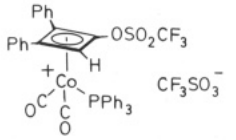
^1H NMR data for the zwitterions **4** are reported in Table III. The most notable feature concerns the observation of long-range coupling from ^{19}F to the ring proton at position R^3. Notably the protons at position R^2 in **4d** and **4f** do not show this coupling nor do methyl or *t*-Bu groups adjacent to the OBF_3 group in **4d** or **4e**. It is unclear whether this is a "through-space" or "through-bond" coupling,[25] although the lack of observable coupling to adjacent Me or *t*-Bu groups might be construed to favor the latter mechanism.

Compound **2b** reacted rapidly and quantitatively with $PhCO^+SbF_6^-$ to afford the cyclobutadiene derivative **6**.



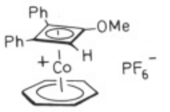
6.

The low value of the ester carbonyl stretching frequency (1605 cm^{-1}) is noteworthy in this compound; we have suggested previously that this may be due to weak interaction with the cationic metal center.[18] Attempts to synthesize the corresponding acetoxycyclobutadiene derivatives by the reaction of either **2a** or **2b** with $CH_3CO^+BF_4^-$ (generated in situ from CH_3COCl and $AgBF_4$) led only to the BF_3 adducts **4g** and **4b**, respectively; only **4b** could be isolated from solution (vide supra). These latter two compounds were erroneously identified as the acetoxycyclobutadiene derivatives in a preliminary communication.[18] Similarly, **2b** reacted rapidly with trifluoromethanesulfonic anhydride to afford the cationic complex **7**; this compound underwent rapid hydrolysis in solution to afford **2b**.

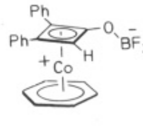


7.

The carbonyl ligands in complex **2a** were sufficiently labile to undergo displacement by benzene at 80 °C to afford the sandwich compound **8**. A similar sandwich complex $[Co(\eta\text{-}C_6H_6)(\eta\text{-}C_4Ph_4)]^+Br^-$ has been synthesized from the reaction of $[Co(\eta\text{-}C_4Ph_4)(CO)_2Br]$ with $AlCl_3$ in the presence of benzene.[26] Similarly, the reaction of **2a** with $BF_3{\cdot}OEt_2$ in refluxing benzene afforded the zwitterionic sandwich **9**, presumably via the intermediacy of **4g**.



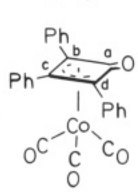
8.



9.

X-ray Crystallographic Study of Compound 2i. A stereoview of the cationic portion of **2i**, together with the atom numbering scheme, is shown in Figure 1. Atomic positional parameters, with corresponding esd's as estimated from the least-squares inverse matrix, are presented in Table IV. Bond lengths and bond angles appear in Table V. Observed and calculated structure factor amplitudes, thermal parameters for nonhydrogen atoms, and hydrogen coordinates are available as supplementary material.[27]

The molecular structure of **2i** can be compared and contrasted with that of the η^3-cyclobutenonyl complex **10**.[28]



10.

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(25) Emsley, J. W.; Phillips, L.; Wray, J. "Fluorine Coupling Constants"; Pergamon Press: Oxford, 1977.

(26) Efraty, A.; Maitlis, P. M. *J. Am. Chem. Soc.* **1967**, *89*, 3744–3750.

(27) See paragraph at end of paper regarding supplementary material.

(28) Potenza, J.; Johnson, R.; Mastropaolo, D.; Efraty, A. *J. Organomet. Chem.* **1974**, *64*, C13–C15.

Table IV. Fractional Coordinates for Nonhydrogen Atoms[a]

atom	*x*	*y*	*z*
CO	0.21095 (6)	0.35836 (9)	0.46366 (6)
P	−0.1602 (1)	0.2677 (2)	0.3118 (1)
F(1)	−0.2068 (3)	0.2174 (5)	0.2030 (2)
F(2)	−0.1830 (3)	0.4475 (4)	0.2810 (3)
F(3)	−0.0568 (2)	0.2819 (5)	0.2985 (3)
F(4)	−0.1127 (3)	0.3197 (5)	0.4204 (2)
F(5)	−0.1388 (3)	0.0873 (4)	0.3410 (3)
F(6)	−0.2626 (3)	0.2509 (5)	0.3248 (3)
O(1)	0.1737 (3)	−0.0116 (5)	0.4564 (3)
O(2)	0.1312 (3)	0.2540 (5)	0.6132 (3)
O(3)	0.0517 (3)	0.5764 (5)	0.3631 (3)
O(4)	0.3656 (4)	0.5854 (6)	0.5563 (4)
C(1)	0.2098 (4)	0.1099 (6)	0.4240 (4)
C(2)	0.3063 (4)	0.1786 (6)	0.4613 (4)
C(3)	0.2794 (5)	0.2808 (7)	0.3756 (4)
C(4)	0.1820 (5)	0.2170 (7)	0.3468 (4)
C(5)	0.3332 (5)	0.3722 (8)	0.3212 (5)
C(6)	0.3942 (4)	0.1335 (7)	0.5369 (4)
C(7)	0.4828 (4)	0.2023 (8)	0.5445 (5)
C(8)	0.5651 (5)	0.1581 (9)	0.6171 (5)
C(9)	0.5604 (5)	0.0442 (9)	0.6828 (5)
C(10)	0.4739 (5)	−0.0269 (9)	0.6752 (5)
C(11)	0.3913 (5)	0.0174 (8)	0.6030 (5)
C(12)	0.0722 (5)	−0.0382 (9)	0.4108 (5)
C(13)	0.1608 (4)	0.2977 (7)	0.5569 (4)
C(14)	0.1127 (5)	0.4954 (7)	0.4000 (4)
C(15)	0.3033 (5)	0.5013 (8)	0.5221 (5)

[a] See Figure 1 for identity of the atoms. Numbers in parentheses are the estimated standard deviations in the units of the least significant digits for the corresponding parameter.

Table V. Bond Lengths (Å) and Bond Angles (Deg)[a]

Bond Lengths

Co-C(1)	2.178 (6)	C(6)-C(11)	1.399 (9)
Co-C(2)	2.074 (6)	C(7)-C(8)	1.379 (11)
Co-C(3)	2.007 (7)	C(8)-C(9)	1.389 (11)
Co-C(4)	2.033 (6)	C(9)-C(10)	1.377 (11)
Co-C(13)	1.845 (6)	C(10)-C(11)	1.380 (10)
Co-C(14)	1.848 (7)	C(12)-O(1)	1.437 (9)
Co-C(15)	1.809 (7)	C(13)-O(2)	1.126 (8)
C(1)-C(2)	1.461 (8)	C(14)-O(3)	1.117 (8)
C(1)-C(4)	1.412 (9)	C(15)-O(4)	1.137 (9)
C(1)-O(1)	1.318 (7)	P-F(1)	1.593 (4)
C(2)-C(3)	1.481 (8)	P-F(2)	1.590 (4)
C(2)-C(6)	1.456 (8)	P-F(3)	1.600 (4)
C(3)-C(4)	1.455 (9)	P-F(4)	1.594 (4)
C(3)-C(5)	1.515 (9)	P-F(5)	1.587 (4)
C(6)-C(7)	1.396 (9)	P-F(6)	1.585 (4)

Bond Angles

C(2)-C(1)-O(1)	128.9 (5)	C(1)-O(1)-C(12)	115.5 (5)
C(2)-C(1)-C(4)	92.1 (5)	C(13)-Co-C(14)	96.9 (3)
C(4)-C(1)-O(1)	138.9 (6)	C(13)-Co-C(15)	104.3 (3)
C(1)-C(2)-C(3)	87.5 (5)	C(14)-Co-C(15)	99.4 (3)
C(1)-C(2)-C(6)	133.7 (5)	F(1)-P-F(2)	89.0 (2)
C(3)-C(2)-C(6)	137.2 (5)	F(2)-P-F(4)	90.5 (2)
C(2)-C(3)-C(4)	89.7 (5)	F(4)-P-F(5)	90.4 (2)
C(2)-C(3)-C(5)	135.9 (6)	F(5)-P-F(1)	90.1 (2)
C(4)-C(3)-C(5)	131.9 (6)	F(1)-P-F(3)	90.0 (2)
C(1)-C(4)-C(3)	90.4 (5)	F(3)-P-F(4)	89.4 (2)
C(2)-C(6)-C(7)	121.2 (6)	F(4)-P-F(6)	91.0 (3)
C(2)-C(6)-C(11)	120.0 (6)	F(6)-P-F(1)	89.7 (2)
C(7)-C(6)-C(11)	118.7 (6)	F(2)-P-F(3)	90.6 (2)
C(6)-C(7)-C(8)	120.2 (6)	F(3)-P-F(5)	89.7 (2)
C(7)-C(8)-C(9)	120.3 (7)	F(5)-P-F(6)	89.5 (2)
C(8)-C(9)-C(10)	120.2 (7)	F(6)-P-F(2)	90.1 (2)
C(9)-C(10)-C(11)	119.7 (7)	F(1)-P-F(4)	179.2 (2)
C(6)-C(11)-C(10)	120.9 (7)	F(2)-P-F(5)	179.1 (3)
Co-C(13)-O(2)	176.9 (5)	F(3)-P-F(6)	179.2 (2)
Co-C(14)-O(3)	177.8 (6)		
Co-C(15)-O(4)	175.1 (6)		

[a] Numbers in parentheses are the estimated standard deviations in the least significant digits. See Figure 1 for identity of the atoms. C-H distances range from 0.76 (6) to 1.10 (6) Å and average 0.94 Å.

The four carbon atoms of the cyclobutadiene ring in **2i** are coplanar to ±0.03 Å,[29] with C(1) lying +0.029 (6) Å, C(2) −0.024 (5) Å, C(3) +0.032 (6) Å, and C(4) −0.035 (6) Å from this plane; the cobalt atom is located at a point −1.792 (1) Å from the plane of the cyclobutadiene ligand. The dihedral angle between the planes C(1)–C(2)–C(3) and C(1)–C(4)–C(3) in **2i** is 6.7°, which is comparable to the corresponding pucker angle of ca. 11° in **10**.[30] The substituent atoms directly bound to the cyclobutadiene ring in **2i** are bent away from the metal: O(1) by 0.147 (4) Å, C(6) by 0.141 (6) Å, and C(5) by a significantly larger 0.435 (7) Å. Similarly the phenyl carbon atoms bound to the cyclobutenonyl ring of **10** are reported to be displaced out of the C(b)–C(c)–C(d) plane by 0.08–0.40 Å.[28] It is interesting that the methoxy carbon atom C(12) in **2i** is actually coplanar with the cyclobutadiene ring carbon atoms, lying 0.002 (7) Å from the plane of the ring, and is therefore closer to the metal atom than is the oxygen atom O(1) of the methoxy group. The phenyl substituent at C(2) is slightly tipped with the best plane of the phenyl ring making a dihedral angle of 7.7° with that of the cyclobutadiene ligand. This compares favorably with the value of ca. 10° for the corresponding angle between the phenyl ring at position C(b) or C(d) and the C(b)–C(c)–C(d) plane in **10**.[28]

The cyclobutadiene ring in **2i** is certainly not square. The C(1)–C(2) and C(3)–C(4) distances are identical [mean value 1.458 (9) Å], but the C(1)–C(4) distance is significantly shorter at 1.412 (9) Å and the C(2)–C(3) distance an appreciably longer 1.481 (8) Å. There is no obvious reason why this should be so and these distortions can be contrasted with the more symmetrical ring in the albeit less precise structure of **10**.

There are some interesting differences in the cobalt to ring carbon distances in **2i**; the metal is significantly closer to C(3) [2.007 (7) Å] than to C(2) or C(4) [2.033 (6) and 2.074 (6) Å, respectively] and is even farther from C(1) [2.178 (6) Å]. This pattern is quite similar to that found in **10**, where the Co–C(c) distance[30] is 1.999 (17) Å, Co–C(b) is 2.117 (17) Å, Co–C(d) is 2.104 (17) Å, and Co–C(a) is 2.405 (17) Å;[28] C(a) is displaced away from the metal by puckering of the cyclobutenonyl ring (vide supra). Notably, if C(a) were coplanar with the other three ring carbon atoms in **10**, the Co–C(a) distance would drop by ca. 0.2 Å to ca. 2.2 Å, which is identical with that observed for the Co–C(1) distance in **2i**. Thus it appears that the transformation of a η^3-cyclobutenonyl ligand to a η^4-methoxycyclobutadiene ligand by alkylation at oxygen may simply involve some loss of ring pucker with the formerly ketonic carbon moving down toward the metal to become coplanar with the other three carbons of the four-membered ring; no other significant reorganization of the metal–ring bonding appears to occur.

Experimental Section

General Data. IR spectra were run in CH_2Cl_2 solution on a Perkin-Elmer PE257 or 599 instrument and were calibrated against the 1601-cm^{-1} band of polystyrene. ^1H NMR (60 MHz), ^{13}C NMR (15 MHz), and ^{19}F NMR (56.3 MHz) spectra were run on a JEOL FX-60Q spectrometer. ^1H and ^{13}C chemical shifts are

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(29) The equation for this weighted best plane is $0.5025x - 0.6856y - 0.5267z + 3.2976 = 0$, referred to an orthonormal (Cartesian) coordinate system with axes in the direction of crystallographic *a*, *b*, and *c**.

(30) Compound **10** contains two molecules per asymmetric unit. The distances and angles quoted are mean values of those given for the individual molecules.[28]

reported in parts per million downfield from the proton or carbon resonances of internal Me_4Si, and ^{19}F chemical shifts are given in parts per million upfield from internal $CFCl_3$. Microanalyses were carried out by Spang, Eagle Harbor, MI.

Solvents were dried by distillation from sodium benzophenone ketyl, except for CH_2Cl_2, which was distilled from P_4O_{10}. All reactions were run in oven-dried glassware under an atmosphere of dry nitrogen.

General Procedure for the Preparation of Methoxycyclobutadiene Complexes 2. A sample of the η^3-cyclobutenonyl complex 1 (0.2–5 mmol) was dissolved in dry CH_2Cl_2 (10–50 mL), and an equimolar amount of trimethyloxonium hexafluorophosphate (Aldrich) was added. The reaction mixture was stirred at room temperature until all the oxonium salt had dissolved, and IR monitoring indicated that conversion to 2 was complete (4–24 h), and the solvent was removed in vacuo. The residue was taken up in a minimum volume of CH_2Cl_2, filtered through filter aid, and treated with anhydrous Et_2O until the solution became cloudy. Crystals were allowed to form, first at room temperature and then at −30 °C, affording analytically pure samples after filtration and vacuum drying. Satisfactory microanalyses (±0.4% from theory for C and H) were obtained for all compounds reported. Although the reactions clearly were quantitative by IR, the yields quoted are for analytically pure, recrystallized samples. Poor yields were usually obtained on small scale reactions.

The following compounds were prepared in this manner.

(η-2,3-Diphenyl-1-methoxycyclobutadiene)tricarbonylcobalt(1+) hexafluorophosphate, 2a: 85%, mp 120 °C dec; ν_{CO} 2128 (s), 2085 (br s) cm^{-1}.

Anal. Calcd for $C_{20}H_{14}CoF_6O_4P$: C, 46.00; H, 2.70. Found: C, 46.07; H, 2.73.

(η-2,3-Diphenyl-1-methoxycyclobutadiene)dicarbonyl(triphenylphosphine)cobalt(1+) hexafluorophosphate, 2b: 79%; mp 110 °C; ν_{CO} 2071 (s), 2035 (s) cm^{-1}.

Anal. Calcd for $C_{37}H_{29}CoF_6O_3P_2$: C, 58.75; H, 3.86. Found: C, 58.84; H, 3.95.

(η-2,3-Diphenyl-1-methoxycyclobutadiene)dicarbonyl(methyldiphenylphosphine)cobalt(1+) hexafluorophosphate, 2c: 45%; mp 96 °C; ν_{CO} 2069 (s), 2033 (s) cm^{-1}.

Anal. Calcd for $C_{32}H_{27}CoF_6O_3P_2$: C, 55.35; H, 3.92. Found: C, 55.07; H, 3.86.

(η-2,3-Diphenyl-1-methoxycyclobutadiene)dicarbonyl(dimethylphenylphosphine)cobalt(1+) hexafluorophosphate, 2d: 49%; mp 150–152 °C; ν_{CO} 2067 (s), 2029 (s) cm^{-1}.

Anal. Calcd for $C_{27}H_{25}CoF_6O_3P_2$: C, 51.28; H, 3.98. Found: C, 51.07; H, 3.99.

(η-2,3-Diphenyl-1-methoxycyclobutadiene)dicarbonyl(triethylphosphine)cobalt (1+) hexafluorophosphate: 50%; mp 135 °C dec; ν_{CO} 2061 (s), 2025 (s) cm^{-1}.

Anal. Calcd for $C_{25}H_{29}CoF_6O_3P_2$: C, 49.04; H, 4.77. Found: C, 48.82; H, 4.70.

(η-2,3-Diethyl-1-methoxycyclobutadiene)tricarbonylcobalt(1+) hexafluorophosphate, 2f: 76%; mp 155 °C dec; ν_{CO} 2123 (s), 2073 (s, br) cm^{-1}.

Anal. Calcd for $C_{12}H_{14}CoF_6O_4P$: C, 33.83; H, 3.29. Found: C, 33.66; H, 3.31.

(η-2,3-Diethyl-1-methoxycyclobutadiene)dicarbonyl(triphenylphosphine)cobalt (1+) hexafluorophosphate, 2g: 73%; mp 145–149 °C; ν_{CO} 2069 (s), 2029 (s) cm^{-1}.

Anal. Calcd for $C_{29}H_{29}CoF_6O_3P_2$: C, 52.74; H, 4.42. Found: C, 52.53; H, 4.25.

(η-1-Methoxy-2-methyl-3-phenylcyclobutadiene)tricarbonylcobalt(1+) hexafluorophosphate, 2h: 37%; mp 138–141 °C; ν_{CO} 2120 (s), 2073 (s, br) cm^{-1}.

Anal. Calcd for $C_{15}H_{12}CoF_6O_4P$: C, 39.24; H, 2.41. Found C, 39.40; H, 2.63.

(η-1-Methoxy-3-methyl-2-phenylcyclobutadiene)tricarbonylcobalt(1+) hexafluorophosphate, 2i: 48%; mp 146–148 °C; ν_{CO} 2120 (s), 2073 (s, br) cm^{-1}.

Anal. Calcd for $C_{15}H_{12}CoF_6O_4P$: C, 39.24; H, 2.41. Found: C, 39.37; H, 2.50.

(η-1-Methoxy-3-methyl-2-phenylcyclobutadiene)dicarbonyl(triphenylphosphine)cobalt(1+) hexafluorophosphate, 2j: 60%; mp 190 °C dec; ν_{CO} 2065 (s), 2026 (s) cm^{-1}.

Anal. Calcd for $C_{32}H_{27}CoF_6O_3P_2$: C, 53.75; H, 4.06. Found: C, 53.93; H, 4.11.

(η-1-Methoxy-2-methyl-4-phenylcyclobutadiene)tricarbonylcobalt(1+) hexafluorophosphate, 2k: 13%; mp 127 °C dec; ν_{CO} 2125 (s), 2081 (s, br) cm^{-1}.

Anal. Calcd $C_{15}H_{12}CoF_6O_4P$: C, 39.24; H, 2.41. Found: C, 39.44; H, 2.67.

(η-2-*tert*-Butyl-1-methoxycyclobutadiene)tricarbonylcobalt(1+) hexafluorophosphate, 2l: 27%; mp 150 °C dec; ν_{CO} 2129 (s), 2081 (s, br) cm^{-1}.

Anal. Calcd for $C_{12}H_{14}CoF_6O_4P$: C, 33.82; H, 3.31. Found: C, 34.02; H, 3.46.

(η-2-*tert*-Butyl-1-methoxycyclobutadiene)dicarbonyltriphenylphosphine)cobalt(1+) hexafluorophosphate, 2m: 44%; mp 160–164 °C; ν_{CO} 2075 (s), 2037 (s) cm^{-1}.

Anal. Calcd for $C_{29}H_{29}CoF_6O_3P_2$: C, 52.74; H, 4.43. Found: C, 53.05; H, 4.60%.

(η-3-*tert*-Butyl-1-methoxycyclobutadiene)dicarbonyl(dimethylphenylphosphine)cobalt(1+) hexafluorophosphate, 2n: 56%; mp 93–94 °C; ν_{CO} 2073 (s), 2033 (s) cm^{-1}.

Anal. Calcd for $C_{19}H_{25}CoF_6O_3P_2$: C, 41.93; H, 4.63. Found: C, 41.82; H, 4.46.

(η-2-*n*-Butyl-1-methoxycyclobutadiene)tricarbonylcobalt(1+) hexafluorophosphate, 2o: 68%; mp 88–89 °C; ν_{CO} 2128 (s), 2076 (s, br) cm^{-1}.

Anal. Calcd for $C_{12}H_{14}CoF_6O_4P$: C, 33.82; H, 3.31. Found: C, 33.74; H, 3.24.

(η-1-Ethoxy-2,3-diphenylcyclobutadiene)tricarbonylcobalt(1+) tetrafluoroborate, 3: 75%; mp 126–129 °C; ν_{CO} 2123 (s), 2077 (s) cm^{-1}, from 1a and triethyloxonium tetrafluoroborate (Aldrich, solution in CH_2Cl_2).

Anal. Calcd for $C_{21}H_{16}BCoF_4O_4$: C, 52.76; H, 3.37. Found: C, 52.78; H, 3.60.

General Procedure for the Preparation of BF_3 Adducts 4. A solution of the appropriate η^3-cyclobutenonyl complex 1 (0.02–0.6 mmol) in CH_2Cl_2 (10–20 mL) was treated with a stoichiometric amount of $BF_3{\cdot}OEt_2$ and stirred (4 h). The solution was evaporated in vacuo; the residue was taken up in a minimum amount of CH_2Cl_2 and filtered through filter aid. A 1:1 ratio mixture of Et_2O/hexane was added until the solution became cloudy, and the mixture was set aside at −30 °C (24 h) to afford the product as yellow crystals. Yields were quantitative by IR spectroscopy. Recrystallized yields are quoted. Satisfactory microanalysis data (C, H) were obtained from all compounds reported.

The following compounds were prepared in this way.

(η-2,3-Diethyl-1-(trifluoroboroxy)cyclobutadienedicarbonyl(triphenylphosphine)cobalt, 4a: 61%; mp 146 °C dec; ν_{CO} 2052 (s), 2012 (s) cm^{-1}; ^{19}F NMR ($CDCl_3$) δ 152.10 (br, s).

Anal. Calcd for $C_{28}H_{26}BCoF_3O_3P$: C, 59.18; H, 4.61. Found: C, 59.07; H, 4.44.

(η-2,3-Diphenyl-1-(trifluoroboroxy)cyclobutadiene)dicarbonyl(triphenylphosphine)cobalt, 4b: 61%; mp 150 °C dec; ν_{CO} 2067 (s), 2025 (s) cm^{-1}; ^{19}F NMR ($CDCl_3$) δ 151.8 (br, s).

Anal. Calcd for $C_{36}H_{26}BCoF_3O_3P$: C, 65.09; H, 3.94. Found: C, 65.14; H, 4.04.

(η-3-Methyl-2-phenyl-1-(trifluoroboroxy)cyclobutadiene)dicarbonyl(triphenylphosphine)cobalt, 4c: 94%, oil; ν_{CO} 2057 (s), 2017 (s) cm^{-1}.

Anal. Calcd for $C_{31}H_{24}BCoF_3O_3P$: C, 61.82; H, 4.02. Found: C, 62.00; H, 4.10.

(η-2-*tert*-Butyl-1-(trifluoroboroxy)cyclobutadiene)dicarbonyl(triphenylphosphine)cobalt, 4d: 83%; mp 175 °C dec; ν_{CO} 2059 (s), 2017 (s) cm^{-1}.

Anal. Calcd for $C_{28}H_{26}BCoF_3O_3P$: C, 59.19; H, 4.61. Found: C, 59.26; H, 4.70.

(η-2-Methyl-3-phenyl-1-(trifluoroboroxy)cyclobutadiene)dicarbonyl(triphenylphosphine)cobalt, 4e: 90%, oil; ν_{CO} 2057 (s), 2017 (s) cm^{-1}.

Anal. Calcd for $C_{31}H_{24}BCoF_3O_3P$: C, 61.82; H, 4.02. Found: C, 62.12; H, 4.12.

(η-2-Methyl-4-phenyl-1-(trifluoroboroxy)cyclobutadiene)dicarbonyl)(triphenylphosphine)cobalt, 4f: 72%, mp 93–95 °C, ν_{CO} 2057 (s), 2017 (s) cm^{-1}.

Anal. Calcd for $C_{31}H_{24}BCoF_3O_3P$: C, 61.82; H, 4.02. Found: C, 61.80; H, 4.00.

Similarly, reaction of **1a** with $BF_3\cdot OEt_2$ in CH_2Cl_2 solution effected complete conversion to **4f** [ν_{CO} 2121 (s), 2081 (s), 2069 (s) cm^{-1}], and an analogous reaction of **1f** yielded a solution of **4g** [ν_{CO} 2115 (s), 2070 (s), 2057 (s) cm^{-1}]; evaporation of these solutions afforded only the starting ketone.

(η-1-(Benzoyloxy)-2,3-diphenylcyclobutadiene)dicarbonyl(triphenylphosphine)cobalt(1+) hexafluoroantimonate, 6. A solution of **1b** (0.18 g, 0.30 mmol) in CH_2Cl_2 (5 mL) was treated with $PhCO^+SbF_6^-$ (Cationics; 0.10 g, 0.30 mmol), and the solution was stirred (4 h). The solvent was removed in vacuo, and the residue was taken up in a minimum amount of CH_2Cl_2, filtered through filter aid, and treated with anhydrous Et_2O to afford **6** as yellow crystals: 0.14 g, 50%; mp 128 °C dec; IR ν_{CO} 2061 (s), 2021 (s), 1605 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.21 (d, J_{PH} = 3.4 Hz, CH), 7.1–7.8 (m, Ph).

Anal. Calcd for $C_{43}H_{31}CoF_6O_4PSb$: C, 55.10; H, 3.33. Found: C, 54.75; H, 3.20.

A similar reaction of **1b** with $CH_3CO^+BF_4^-$ did not afford the expected product but yielded **4b**.

(η-2,3-Diphenyl-1-(trifluoromethanesulfonato)cyclobutadiene)dicarbonyl(triphenylphosphine)cobalt(1+) Trifluoromethanesulfonate, 7. A solution of **1b** (0.88 g, 1.48 mmol) in dry CH_2Cl_2 (50 mL) was treated with trifluoromethanesulfonic anhydride[31] (0.25 mL, 1.48 mmol). The yellow solution turned golden brown and was stirred (0.25 h). The solvent was removed in vacuo and the residue recrystallized from CH_2Cl_2/Et_2O to afford the product as yellow crystals: 1.16 g, 89%; mp 125 °C dec; IR ν_{CO} 2091 (s), 2061 (s) cm^{-1}.

Anal. Calcd for $C_{38}H_{26}CoF_6O_8PS_2$: C, 51.94; H, 2.98. Found: C, 52.27; H, 3.10.

(η-Benzene)(η-2,3-diphenyl-1-methoxycyclobutadiene)cobalt(1+) hexafluorophosphate, 8. A slurry of **2a** (1.59 g, 3.05 mmol) in dry benzene (50 mL) was heated to reflux (4 h). The mixture was cooled and the solvent removed in vacuo. Recrystallization of the residue from CH_2Cl_2/Et_2O afforded the product as yellow-orange crystals: 1.17 g, 74%; mp 136–138 °C; ^1H NMR ($CDCl_3$) δ 3.88 (s, OMe), 5.85 (s, CH), 6.42 (s, η-C_6H_6), 7.2–7.4 (m, Ph); $^{13}C\{^1H\}$ NMR (acetone-d_6) δ 74.39 (OCH_3), 80.88 (CH), 91.03 (CPh), 93.98 (CPh), 114.60 (η-C_6H_6), 143.32, 143.53, 144.42, 144.58, 145.75, 147.01 (Ph).

Anal. Calcd for $C_{23}H_{20}CoF_6OP$: C, 53.50; H, 3.90. Found: C, 53.34; H, 3.88.

(η-Benzene)(η-2,3-diphenyl-1-(trifluoroboroxy)cyclobutadiene)cobalt, 9. A solution of **1a** (0.48 g, 1.33 mmol) in dry benzene (25 mL) was treated with $BF_3\cdot OEt_2$ (1 mL), and the reaction mixture was refluxed (48 h). The solvent was removed in vacuo, and the residue recrystallized from CH_2Cl_2/hexanes to afford the product as yellow crystals: 0.37 g, 67%; mp 208–211 °C; ^1H NMR (acetone-d_6) δ 5.36 (q, J_{FH} = 1.7 Hz, CH), 6.46 (s, η-C_6H_6), 7.2–7.7 (m, Ph).

Anal. Calcd for $C_{22}H_{17}BCoF_3O$: C, 62.30; H, 4.04. Found: C, 62.14; H, 4.01.

X-ray Crystallographic Determination of the Structure of 2i. Crystals of $C_{15}H_{12}CoO_4^+$, PF_6^- were obtained as orange prisms by slow evaporation of ethyl acetate. A suitable crystal was glued to a glass fiber that was attached to the brass pin of a goniometer head. It was then transferred to a Syntex $P2_1$ diffractometer where it was maintained in a stream of cold (−100 °C), dry N_2. Preliminary examination of the crystal with the diffractometer indicated the monoclinic symmetry of space group $P2_1/c$ (No. 14). Crystal data and data collection details are summarized in Table VI. A shutter failure after 2309 reflections (35.1 h) of data collection necessitated shutter repair and monochromator realignment. Analysis of check reflections before and after this interpretaton showed that the intensity had diminished by about 5.4%, and the second block of data was scaled accordingly. The recorded X-ray intensities were reduced and assigned standard deviations (with $p = 0.02$) as described elsewhere.[32]

The structure was solved by heavy-atom procedures and refined by full-matrix least-squares methods.[33] The function minimized in refinement is $\sum w(|F_o| - |F_c|)^2$, where the weight w is $\sigma(|F_o|)^{-2}$, the reciprocal square of the standard deviation of each observation, $|F_o|$. Neutral atom scattering factors for Co, P, F, O, C[34] and H[35] were used in these calculations, and the real ($\Delta f'$) and imaginary ($\Delta f''$) corrections[34] for anomalous scattering of Mo Kα radiation were applied to the Co and P scattering curves. All hydrogen atoms were located in difference density maps except for the three hydrogens on C(5). These methyl hydrogens were unable to be determined reliably and were thus not included in further calculations. Due to their erratic behavior when refinement was attempted, the temperature factor for each hydrogen which was included in the calculation was held constant at a value equal to the final B value for the carbon to which the hydrogen is attached. Least-squares convergence was attained by using only those 2175 reflections with $I_o/\sigma(I_o) > 2.0$ for a structure in which all nonhydrogen atoms were refined anisotropically and hydrogen atoms isotropically, with $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.054$, $R_w = [\sum w(|F_o| - |F_c|]^2/\sum w|F_o|^2]^{1/2} = 0.049$, and standard deviation of an observation of unit weight $= [\sum w(||F_o| - |F_c||)^2/(m - s)]^{1/2} = 1.65$, for $m = 2175$ and $s = 271$ variables. A structure factor calculation using the atomic parameters obtained at convergence with all 3062 reflections gathered during data collection gave R and R_w values of 0.087 and 0.051, respectively.

Table VI. Crystallographic Summary

Crystal Data at −100 °C[a]

empirical formula	$C_{15}H_{12}CoO_4^+$,PF_6^-	γ, deg	90
fw	460.19	V, Å^3	1740
a, Å	14.689 (5)	d_{calcd}, g cm^{-3}	1.058[b]
b, Å	8.444 (2)	cryst system	monoclinic
c, Å	14.865 (5)	space group	$P2_1/c$
α, deg	90	Z	4
β, deg	109.32 (3)	$F(0,0,0)$, e	920

Data Collection at −100 °C

radiation	0.710 69
mode	ω scan
scan range	symmetrically over 1.0° about K$\alpha_{1,2}$ (max)
background	offset 1.0 and −1.0° in ω from K$\alpha_{1,2}$ (max)
scan rate, deg min^{-1}	variable, 2.0–5.0
check reflctns	4 remeasured after every 96 reflections; analysis[c] of these data indicated only random fluctuation in intensity during the 20 h of data collection, except for the discontinuity due to shutter failure and repair (see text).
2θ range, deg	4.0–50.0
total reflections measd	3062
data crystal dimens, mm	0.2 × 0.4 × 0.4
absorption coeff, μ(Mo Kα), cm^{-1}	12.0

[a] Unit cell parameters were obtained by least-squares refinement of the setting angles of 43 reflections with $17.3 < 2\theta < 21.7°$. [b] Owing to scarcity of crystals, an experimental density was not obtained. [c] Henslee, W. H. Davis, R. E. *Acta Crystallogr., Sect. B* **1975**, *B31*, 1511.

In the final cycle of refinement, the largest shifts in nonhydrogen and hydrogen atom parameters were less than 0.3 and 0.7 times a corresponding estimated standard deviation (esd), respectively. The largest peaks on a final difference electron density map were no greater than 0.7 e Å^{-3}.

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Registry No. **1a**, 77818-75-8; **1b**, 81434-76-6; **1c**, 81434-77-7; **1d**, 81434-78-8; **1e**, 81434-79-9; **1f**, 81434-80-2; **1g**, 81434-81-3; **1h**, 81434-82-4; **1i**, 81434-83-5; **1j**, 81434-84-6; **1k**, 81446-87-9; **1l**, 81434-85-7; **1m**, 81434-86-8; **1n**, 81434-87-9; **1o**, 81434-88-0; **2a**, 81434-90-4; **2b**, 81434-92-6; **2c**, 81434-94-8; **2d**, 81434-96-0; **2e**, 81434-98-2; **2f**, 81435-00-9; **2g**, 81446-89-1; **2h**, 81435-02-1; **2i**, 81435-04-3; **2j**, 81435-06-5; **2k**, 81435-08-7; **2l**, 81435-10-1; **2m**, 81435-12-3; **2n**, 81435-14-5; **2o**, 81435-16-7; **3**, 81435-18-9; **4a**, 81435-19-0; **4b**, 81435-20-3; **4c**, 81435-21-4; **4d**, 81446-90-4; **4e**, 81456-85-2; **4f**, 81435-22-5; **4g**, 81435-23-6; **6**, 81435-25-8; **7**, 81456-88-4; **8**, 70236-70-3; **9**, 81435-26-9; $Me_3O^+PF_6^-$, 12116-05-1; $BF_3{\cdot}OEt_2$, 109-63-7; $PhCO^+SbF_6^-$, 5609-80-3; trifluoromethanesulfonic anhydride, 358-23-6.

Supplementary Material Available: Tabulations of observed and calculated structure amplitudes (Supplementary Table 1), anisotropic thermal parameters (Supplementary Table 2), and hydrogen positional and isotropic thermal parameters (Supplementary Table 3) (17 pages). Ordering information is given on any current masthead page.

Preparation, Characterization, and Some Reactions of Bis(tri-*tert*-butylphosphine)hydridoplatinum(II) Complexes

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Treatment of $Pt[P(t\text{-}Bu)_3]_2$ with protic acids, HX, affords the monohydrides *trans*-$PtHX[P(t\text{-}Bu)_3]_2$, **1a** (X = Cl), **1b** (X = Br), **1c** (X = I), and **1d** ($X = O_2CCF_3$). The chlorohydride **1a** is easily converted into the bromo, nitrato **1e** ($X = ONO_2$), and the cyano **1f** (X = CN) analogues by metathesis. The dihydride *trans*-$PtH_2[P(t\text{-}Bu)_3]_2$, **2**, is obtained from the treatment of **1a** with $NaBH_4$ in THF. The monohydrides **1a–e** undergo intramolecular metalation, at room temperature, to give the metalated complexes *trans*-$PtX[P(t\text{-}Bu)_2CMe_2CH_2]P(t\text{-}Bu)_3$, **3a** (X = Cl), **3b** (X = Br), **3c** (X = I), **3d** ($X = O_2CCF_3$), and **3e** ($X = ONO_2$). The complexes **3a–c** readily lose $P(t\text{-}Bu)_3$ to afford the dinuclear complexes $[Pt(\mu\text{-}X)\text{-}\{P(t\text{-}Bu)_2CMe_2CH_2\}]_2$, **4a** (X = Cl), **4b** (X = Br), and **4c** (X = I). The cyanohydride **1f** and the dihydride **2** do not undergo intramolecular metalation. The hydrides **1a–e** undergo reductive elimination, in the presence of a base, to give $Pt[P(t\text{-}Bu)_3]_2$; **1f** and **2** are unaffected under similar conditions. The dihydride **2** is converted into **1a** upon treatment with HCl or CCl_4; **1c** is obtained upon treatment with I_2. Alcohol or phenols react with **2** to give dihydrogen and $Pt[P(t\text{-}Bu)_3]_2$; no reaction occurs with **1a** under similar conditions. The monohydrides **1a–e** react reversibly with CO to give *trans*-$[PtH(CO)\{P(t\text{-}Bu)_3\}_2]X$, **5**, which can be isolated as salts with BF_4^- and PF_6^- as counteranions. The dihydride **2** reacts with CO and *t*-BuNC to afford $Pt_3(CO)_3[P(t\text{-}Bu)_3]_3$, **6**, and $Pt_3[\mu\text{-}CN(t\text{-}Bu)]_3[CN(t\text{-}Bu)]_3$, **7**, respectively.

Introduction

In the course of our investigations[1-3] on reactions of tri-*tert*-butylphosphine with platinum(II) it was discovered that treatment of the phosphine with potassium tetrachloroplatinate(II) in alkaline ethanol affords the two-coordinate complex *trans*-$Pt[P(t\text{-}Bu)_3]_2$ in a very high yield. Although *trans*-$Pt[P(t\text{-}Bu)_3]_2$ had been prepared earlier[4] from the treatment of the phosphine with $Pt(COD)_2$[5] (COD = 1,5-cyclooctadiene), its chemical reactivity had remained unexplored. The discovery of the very facile synthesis of *trans*-$Pt[P(t\text{-}Bu)_3]_2$ enabled us to investigate its chemical reactivity toward a variety of substrates,[2,3] including protic acids. These investigations have shown that, contrary to the views of previous investigators,[4,6] *trans*-$Pt[P(t\text{-}Bu)_3]_2$ readily undergoes oxidative addition as well as ligand substitution reactions. Oxidative addition reactions of *trans*-$Pt[P(t\text{-}Bu)_3]_2$ with haloalkanes and iodine and its ligand substitution reaction with isocyanides and carbon monoxide have been reported recently.[3] Reactions of strong protic acids (HCl, HBr, HI, and CF_3CO_2H) with *trans*-$Pt[P(t\text{-}Bu)_3]_2$ and the characterization and some chemical reactions of the resulting hydridoplatinum(II) complexes are reported herein. A preliminary communication[7] on this work has appeared.

Platinum(II) hydrides have played an important role in the development of the chemistry of transition metal hydrides. Soon after the discovery[8] of the first stable platinum hydride *trans*-$PtHCl(PEt_3)_2$, there has been rapid development in the chemistry of transition metal hydrides.[9-17] Many monohydridoplatinum(II) complexes[18,19]

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