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Preliminary communication

CATIONIC COBALT(I) CARBONYL COMPOUNDS CONTAINING COMPLEXED CYCLOBUTADIENES

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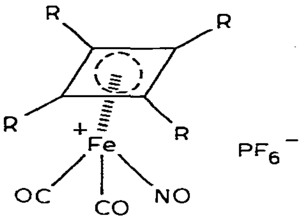
Summary

The first examples of cationic carbonyl complexes of cobalt-containing substituted cyclobutadiene ligands are reported. The carbon monoxide ligands in these complexes are labile, and can be displaced by benzene.

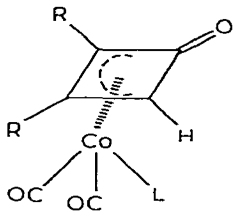
Transition metal complexes of cyclobutadiene and its substituted analogs have long intrigued chemists, ever since the prediction that such compounds should be stable [1]. While a great deal of effort has been expended in the synthesis and characterization of cyclobutadienemetal compounds [1], it is surprising that very few examples of cationic complexes containing cyclobutadiene ligands have been reported [2—5]. Indeed only a single type of cationic metal carbonyl complex (I) containing a cyclobutadiene ligand has been prepared [2]. We here report the preparation and characterization of a series of stable, cationic carbonyl complexes of cobalt(I)-containing substituted cyclobutadiene ligands.

We have recently described a ready synthesis of the cyclobutenonyl complexes (II) and have described the bonding in these compounds as being best represented by a resonance hybrid of the two canonical forms II and III [6]. Introduction of good σ-donor ligands on the metal (L = PR_3) appears to increase the contribution of the zwitterionic form III to the overall structure [6]. The nucleophilicity of the ketone oxygen is revealed in the following reactions.

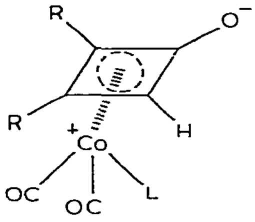
Reaction of the diphenyl substituted complex IIa (ν(CO) (CH_2Cl_2) 2090s, 2035s, 1709m cm^{-1}) with a stoichiometric amount of $Me_3O^+PF_6^-$ (CH_2Cl_2, 25°C, 4 h) affords a quantitative yield of the cationic 2,3-diphenyl-1-methoxycyclobutadiene complex (IVa) as evidenced by infrared monitoring of the reaction mixture. From this solution, on treatment with diethyl ether, complex IVa was obtained as air-stable, yellow crystals (85%; m.p. 120°C, dec.; ν(CO) (CH_2Cl_2) 2128s, 2085s cm^{-1}). Similarly, complex IIb afforded the cationic complex IVb as air-stable, yellow crystals (79%; m.p. 110°C, dec., ν(CO) (CH_2Cl_2)



(I, R = H, Me)

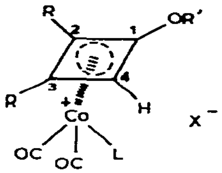


(IIa, R = Ph; L = CO;
IIb, R = Ph; L = PPh$_3$;
IIc, R = Ph; L = PPh$_2$Me;
IId, R = Ph; L = PMe$_2$Ph;
IIe, R = Ph; L = PEt$_3$;
IIf, R = Et; L = CO;
IIg, R = Et; L = PPh$_3$)

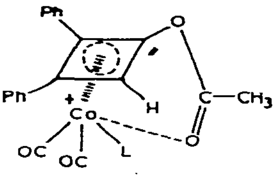


(III)

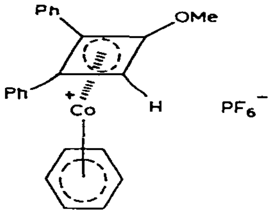
2071s, 2035s cm^{-1})*. The cationic cyclobutadiene complexes IVc—IVe were all obtained in an analogous fashion from the appropriate precursors IIc--IIe. The 1-ethoxy-2,3-diphenylcyclobutadiene complex (IVf) (m.p. 126—129°C, ν(CO) (CH_2Cl_2) 2123s, 2077s cm^{-1}) was similarly synthesized from IIa and $Et_3O^+BF_4^-$, while treatment of IIf and IIg with $Me_3O^+PF_6^-$ afforded, respectively, the 2,3-di-



(IVa, R = Ph; L = CO; R' = Me; X = PF$_6$;
IVb, R = Ph; L = PPh$_3$; R' = Me; X = PF$_6$;
IVc, R = Ph; L = PPh$_2$Me; R' = Me; X = PF$_6$;
IVd, R = Ph; L = PMe$_2$Ph; R' = Me; X = PF$_6$;
IVe, R = Ph; L = PEt$_3$; R' = Me; X = PF$_6$;
IVf, R = Ph; L = CO; R' = Et; X = BF$_4$;
IVg, R = Et; L = CO; R' = Me; X = PF$_6$;
IVh, R = Et; L = PPh$_3$; R' = Me; X = PF$_6$;
IVi, R = Ph; L = PPh$_3$; R' = PhCO; X = SbF$_6$;
IVj, R = Ph; L = PPh$_3$; R' = MeCO; X = BF$_4$;
IVk, R = Ph; L = CO; R' = MeCO; X = BF$_4$)



(V)



(VI)

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*Satisfactory microanalytical data have been obtained for all compounds. ^{1}H and ^{13}C NMR data for representative complexes IV:
(IVa; ^{1}H NMR ($CDCl_3$) δ 7.3—7.7m, (Ph), 6.59s (H), 4.23s ppm (OMe); ^{13}C NMR (acetone-d_6) δ 146—79 (C(1)), 88.31 (C(3)), 82.32 (C(2)), 66.55 (C(4)), 63.05 ppm (O$\underline{Me}$)); (IVb; ^{1}H NMR ($CDCl_3$) δ 7.3—7.6m (Ph), 6.06d, J(P—H) 3.2 Hz (H), 3.82s ppm (OMe); ^{13}C NMR (acetone-d_6) δ 143.93 (C(1)), 79.30 (C(2)), 65.78 (C(3)), 65.33 (C(4)), 62.30 ppm (O$\underline{Me}$), no coupling of ^{31}P to any of the ring carbons is observed); (IVd, ^{1}H NMR ($CDCl_3$), δ 7.2—7.4m (Ph), 5.97d, J(P—H) 5.2 Hz (H), 4.01s (O$\underline{Me}$), 1.88d, J(P—H) 10 Hz (P—Me), 1.71d ppm, J(P—H) 10 Hz (P—Me)); (IVg: ^{1}H NMR ($CDCl_3$) δ 6.05s $\overline{(H)}$, 4.03s (OMe), 2.17m (CH_2), 1.27t, J 7 Hz (Me), 1.11t ppm, J 7 Hz (Me)); (IVi: ^{1}H NMR ($CDCl_3$) δ 7.1—7.7m (Ph), 5.21d ppm, J(P—H) 3.5 Hz (H)).

ethyl-1-methoxycyclobutadiene complexes IVg (ν(CO) (CH_2Cl_2) 2123s, 2073s cm^{-1}) and IVh (ν(CO) (CH_2Cl_2) 2069s, 2029s cm^{-1})*.

The cyclobutenonyl complex IVb also reacted readily with $PhCO^+SbF_6^-$, in CH_2Cl_2 solution, to afford IVi (m.p. 128°C dec., ν(CO) (CH_2Cl_2) 2061s, 2021s, 1605m cm^{-1}). Similar compounds IVj (ν(CO) (CH_2Cl_2) 2113s, 2073s, 2061s, 1609m cm^{-1}) and IVk (ν(CO) 2061s, 2021s, 1585m cm^{-1}) were obtained by the reaction of IVb or IVa with $MeCO^+BF_4^-$. These acyloxy compounds are significantly less stable than their alkoxy analogs, and appear to regenerate the starting cyclobutenonyl complexes on standing in solution.

The remarkably low values for the stretching frequency of the acyloxy carbonyl function in IVi—IVk are noteworthy, and may reflect an interaction of the pendant carbonyl oxygen with the cationic metal center, of the type shown as V. This feature is under further investigation**.

The new cationic cyclobutadiene compounds IV are all air-stable crystalline solids; in contrast, acyclic analogs of IV of the type (η^4-1,3-diene)$Co(CO)_3^+$ have been reported to be extremely unstable species [8]. However, the carbonyl ligands in IVa are extremely labile towards substitution. Warming a solution of IVa in benzene effects complete displacement of all three CO ligands, to afford the cationic sandwich compound VI (74%; m.p. 136—138°C; ^{1}H NMR (acetone-d_6) δ 7.2—7.4m (Ph), 6.42s (C_6H_6), 5.85s (H), 3.88s ppm (OMe)). Examples of this general type of cationic sandwich compound have been previously reported [4].

Further studies of the chemistry of these new compounds particularly their interactions with nucleophiles, are currently in progress.

Acknowledgement

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*The protonation of the ketonic oxygen in an analog of IVa has also been accomplished [7].

**Postulation of such an interaction may well be further substantiated by the observation of three terminal CO stretching frequencies in the IR spectrum of IVk, characteristic of C_s local symmetry. In contrast, the IR spectrum of IVa exhibits only two CO stretching frequencies characteristic of local C_{3v} symmetry. We are grateful to a referee for this suggestion.