Michelle Mellea for experimental assistance, and R.H.C. thanks the A. P. Sloan and the Henry and Camille Dreyfus Foundations for fellowships.

Registry No. 2a, 12112-67-3; **2b**, 84500-08-3; **3b** (L = PPh₃) BF₄, 84500-10-7; **3b** (L₂ = dpe) PF₆, 84500-15-2; **3b** (L₂ = dpp) PF_6 , 84500-19-6; **3b** (L = PMePh₂)PF₆, 84500-23-2; **4b** (L = PPh₃) BF₄, 84500-12-9; 4b (L₂ = dpe) PF₆, 84500-17-4; 4b (L₂ = dpp) PF_6 , 84581-01-1; 5b (L = PPh₃) BF_4 , 84580-15-4; 6b (L = PPh₃), 84500-13-0; 7b (L₂ = dpp) PF₆, 84500-21-0; 7b (L = PMePh₂) PF₆, 84500-25-4; [Ir(dct)(P{OEt}₃)₃]PF₆, 84500-27-6; [Rh(dct)Cl]₂, 84500-28-7; [Rh(dct)(PPh₃)₂]PF₆, 84500-30-1; cis,trans-[RhH₂-(dct)(PPh₃)₂]PF₆, 84500-32-3; cis,trans-[IrH₂(Me₂CO)₂(PPh₃)₂]-BF₄, 82582-67-0; [Rh(Cod)Cl]₂, 12092-47-6.

X-ray Crystal Structure of the Mononuclear Tris(trimethy) phosphite)(maleic anhydride)cobalt(0) Complex

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The crystal structure of a new mononuclear cobalt(0) complex with trimethyl phosphite and maleic anhydride (MA) ligands has been determined from X-ray diffractometer data. The crystals are monoclinic of space group $P2_1/c$ with Z = 4 in a unit cell of dimensions a = 9.517 (4) Å, b = 15.432 (14) Å, c = 16.915(8) Å, and $\beta = 113.17$ (6)°. The structure was solved by direct and Fourier methods and refined by full-matrix least-squares techniques to R = 0.063 for 2726 independent reflections. The metal is linked to three P atoms of the trimethyl phosphite groups and to the CH=CH moiety of MA. The molecular structure of C_1 symmetry contains a pseudotetrahedrally coordinated Co atom with bond distances Co-P(mean) = 2.172 (2) Å, Co-C(olefinic)(mean) = 2.033 (7) Å, and Co-X = 1.898 Å and bond angles P-Co-P(mean) = 99.4 (4)° and P-Co-X 117.4° (X is the midpoint of the olefinic bond). The parameters and bonding of the (trimethyl phosphite)cobalt part of the complex are standard with a mean P-O distance of 1.594 (6) Å and indicates a certain degree of π bonding. The mean O–C bond length is 1.443 (12) Å; Co–P–O angles average to 117.1 (2)° and O–P–O to 100.6 (5)°. The bond lengths in the MA ring (with C_s symmetry) indicate strong π -electron delocalization, in accordance with the large decrease in ν (C=O) from 1780 and 1850 cm⁻¹ in free MA to 1722 and 1787 cm⁻¹ in the complex.

Introduction

Cobalt(0) complexes are catalytically active in hydrogenation, carbonylation, and oligo- and polymerization reactions. As part of the studies on the reactivity and structure of mononuclear d⁹ metal complexes,¹⁻⁴ the intermediate I has been isolated and characterized.



Various mono- and polynuclear complexes are easily formed by partial or total displacement in I,⁵ as shown in Figure 1. Of particular interest is the synthetic route to compounds II and III, as cobalt complexes with phosphitic ligands are known to be extremely active and selective hydrogenation catalysts.⁶⁻⁸ In the presence of unsaturated ligands, these complexes allow for electron delocalization that may lead to interesting properties in terms of activity and selectivity. The elucidation of the structures of such complexes is therefore useful not only in establishing the nature of the coordination around cobalt(0) but also in gaining a better insight into the role of the metal in catalysis. Since only rather few examples of mononuclear d⁹ complexes of cobalt have been prepared^{4,9-13} and in view of the paucity of molecular structural data,^{4,12} an X-ray study of tris(trimethyl phosphite)(maleic anhydride)cobalt(0) (COCA) was undertaken.

Experimental Section

Preparation. COCA was prepared by the total ligand displacement reaction involving addition of 5.0 g (40 mmol) of trimethyl phosphite and 1.0 g (10 mmol) of maleic anhydride to 4.85 g (10 mmol) of a toluene solution (50 mL) of bis(ethyl fumarate)bis(acetonitrile)cobalt(0) under continuous stirring until complete dissolution of the anhydride:

$$Co(CH_3CN)_2L_2 + 3P(OCH_3)_3 + MA \rightarrow [P(OCH_3)_3]_3CoMA + 2L + 2CH_3CN$$

L = ethyl fumarate; MA = maleic anhydride

(1) Agnès, G.; Chiusoli, C. P.; Cometti, G. Chem. Commun., 1968, 1515. (2) Agnès, G.; Cometti, G. Organomet. Chem. Synth. 1970/1972, 1, 185.

- (6) Rakowski, M. C.; Muetterties, E. L. J. Am. Chem. Soc. 1977, 99, 739
- (7) Hirsekorn, F. J.; Rakowski, M. C.; Muetterties, E. L. J. Am. Chem. Soc. 1975, 97, 237.
 - (8) Gosser, L. W. Inorg. Chem. 1976, 15, 1348.
- (a) Gossel, L. W. Morg. Chem., 1570, 154, 1645.
 (b) Klein, H. F. Angew. Chem., Int. Ed. Engl. 1971, 10, 343.
 (10) Chatt, J.; Hart, F. A.; Rosevear, D. T. J. Chem. Soc. 1961, 5504.
 (11) Kruck, T.; Lang, W. Z. Anorg. Allg. Chem. 1966, 343, 181.
 (12) Ward, D. L.; Caughlan, C. N.; Voecks, G. E.; Jennings, P. W. Acta
- Cyrstallogr., Sect. B 1972, B28, 1949.
- (13) Klein, H. F. Angew. Chem., Int. Ed. Engl. 1980, 19, 362.

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Figure 1. Various mono- and polynuclear complexes formed by partial or total displacement in I: N N, 1,10-phenanthroline; \searrow , dialkylfumarate; $R = CH_3$, C_2H_5 , $CH(CH_3)_2$.

After removal of the solvent under vacuum and repeated washing of the residue with n-hexane, 5.0 g of a dark red solid was obtained. The complex is air sensitive, and all manipulations were carried out in inert atmosphere; solvents were outgassed before use. The complex was recrystallized from toluene as dark red prisms in almost quantitative yield (mp 134-135 °C). Microanalytical data and cryoscopic determinations of the molecular weight in benzene are consistent with the above-mentioned mononuclear nature of the molecules. Considerable NMR line broadening shows that COCA is paramagnetic. The EPR spectrum of the powdered sample of COCA (at 298 K) shows a broad signal centered at giso ≈ 2.10 due to the d^9 system with s = 1/2. X-ray analysis: $C_{13}H_{29}CoO_{12}P_3$: $M_r = 529.22$; monoclinic; a

= 9.517 (4) Å, b = 15.432 (14) Å, c = 16.915 (8) Å; $\beta = 113.17$ (6)°; $V = 2283.9 \text{ Å}^3$; $D_{\text{calcd}} = 1.54 \text{ g} \cdot \text{cm}^{-1}$; Z = 4; space group $P2_1/c$ (No. 14) from systematic absences (0k0) for k odd and (h0l) for l odd; F(000) = 1100.

Dark red crystals of COCA were examined in nitrogen-filled Lindemann glass capillary tubes. Accurate cell dimensions and an orientation matrix were determined by a least-squares fit of χ , ϕ , ω , and 2θ values of 12 independent reflections using a Picker FACS-1 four-circle diffractometer. Intensity data were collected with a parallelepiped crystal $(0.4 \times 0.4 \times 0.7 \text{ mm})$ mounted with b along the ϕ axes of the diffractometer using Zr-filtered Mo K α radiation, a 2θ scan rate of 1° min⁻¹, and scan range of 2.0–2.5° (for $K(\alpha_1 - \alpha_2)$ separation). Background counts of 10 s were measured at each end of every 2θ scan. Three standard reflections were monitored after every 50 reflections for scaling purposes; their intensities were constant throughout. Of the 4018 independent reflections measured (up to $2\theta = 50^{\circ}$) 2726 were judged to be observed with $I \geq 2.5\sigma$ ($\sigma = [N_{\rm s} + (t_{\rm s}/t_{\rm b})^2 N_{\rm b}]^{1/2},$ where $N_{\rm s}$ is the total peak count during the time of scanning, t_{a} , and t_{b} is the time spent in measuring the $N_{\rm b}$ background counts). An arbitrary intensity of 0.5 of the observable limit was assigned to each of the nonsignificant reflections. Intensities were corrected for Lorentz and polarization effects but not for absorption (µ(Mo $K\alpha$) = 10.65 cm⁻¹).

The structure was solved by direct methods (MULTAN¹⁴). The E map computed for the phase solution with the highest combined figure of merit gave the positions of the cobalt atom and most of the non-hydrogen atoms. The positions of the remaining atoms were obtained from a subsequent ΔF synthesis. Fully anisotropic refinement of all the non-hydrogen atoms gave an R factor of 0.074. H atoms were introduced in fixed positions, on stereochemical grounds (C–H = 1.0 Å) and in agreement with a ΔF synthesis. The B value of each H atom was set at 5.0 $Å^2$. Refinement converged to R = 0.063 for the 2726 observed reflections. The





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Figure 2. View of tris(trimethyl phosphite)(maleic anhydride)cobalt(0) indicating the atom labeling scheme and 30% probability thermal vibration ellipsoids.



Figure 3. Molecular structure of tris(trimethyl phosphite)(maleic anhydride)cobalt(0) viewed onto the anhydride ligand plane. Principle distances to this plane: P(1), 3.12 Å; P(2), 1.84 Å; P(3), 3.15 Å; Co, 1.88 Å.



Figure 4. Molecular structure of tris(trimethyl phosphite)(maleic anhydride)cobalt(0) viewed onto the C(2)C(4)P(1)P(3) plane.

final shifts of the atomic parameters were negligible and all well below the corresponding σ . The final ΔF synthesis was also featureless.

Positional and thermal parameters of the non-hydrogen atoms were refined with the least-squares program of Immirzi.¹⁵ Atomic scattering factors were calculated according to ref 16 and 17.

⁽¹⁵⁾ Immirzi, A. Ric. Sci. 1967, 37, 743.



🕒 Co 🖨 Р

Figure 5. Packing arrangement of the tris(trimethyl phosphite)(maleic anhydride)cobalt(0) molecules viewed down the a axis.

Cruickshank's¹⁸ weighting scheme, $1/w = A + B|F_0| + C|F_0|^2$, was used, where $A = 2F_{o}(\min)$, B = 1.0, and $C = 2/F_{o}(\max)$. The final coordinates are listed in Table I and the bond lengths and angles in Table II. Figures 2-4 show views of COCA, together with the labeling scheme and the thermal vibration ellipsoids of the non-hydrogen atoms.¹⁹ The packing of the structure components in the unit cell is shown in Figure 5.

Results and Discussion

The crystal structure of COCA consists in the packing of discrete mononuclear molecules separated by van der Waals forces (Figure 5). The cobalt metal is linked to the three phosphorus atoms of the trimethyl phosphite groups and the CH_2 =CH₂ moiety of the maleic anhydride unit (Figure 2).

The molecular structure (C_1 symmetry) consists of a pseudotetrahedrally coordinated Co atom, assuming one coordination site for the olefinic ligand, with the olefin plane nearly perpendicular to C(2), C(4), P(1), and P(3)(Figure 4). The mean Co-P bond length of 2.172 (2) Å (range 2.153-2.198 Å) agrees with that of the mononuclear hydridodinitrogentris(triphenylphosphine)cobalt(I) complex (2.167 Å)²⁰ and is at the lower bound of the usual Co-P range (2.05–2.55 Å), denoting strong π bonding. The fact that the Co-P bond is significantly (about 0.1 Å) shorter than the analogous metal-phosphine bond is rationalized either by π -bonding capability of the phosphite ligand being greater than that of phosphine ligands²¹ or by the minor steric requirements as compared to phos-

(21) Verkade, J. G. Coord. Chem. Rev. 1972, 9, 1.

phines.²² The mean Co–C(olefinic) distance of 2.033 (7) Å (Co-X of 1.898 Å; X is the midpoint of the olefinic bond) is close to the values of 2.060 (9) and 2.084 (4) Å of bis-(ethyl fumarate)bis(acetonitrile)cobalt(0)⁴ and trans-bis- $(\mu$ -carbonyl)bis $(\pi$ -2,3-cis-dimethylbutadiene)carbonylcobalt,²³ respectively, and within the usual range of 1.90–2.10 Å for π bonding.

The mean bond angles P-Co-P and P-Co-X are 99.4 (4) and 117.4°, respectively. Nearly tetrahedral symmetry is known for some cobalt(0) complexes such as dicarbonylnitrosyl(triphenylphosphine)cobalt(0)¹² in which the metal forms σ bonds. In this case the Co-P distance is significantly larger (2.224 (1) Å) than in COCA (2.172 (2) Å), where the metal forms one π and three σ bonds. Angular distortions around cobalt depend on the π -accepting abilities of the ligand and the nonbonded repulsions. The latter are smaller for the nonbulky $P(OCH_3)_3$. Typical short values are P(2)...C(2) = 3.30 Å, P(2)...C(4)= 3.34 Å, P(3)...C(1) = 3.46 Å, O(22)...H(312) = 2.49 Å, and H(212) - H(113) = 2.53 Å.

Viewing down the maleic anhydride (MA) plane (Figure 3), the coordination of COCA may also be described as a deformed tetragonal pyramid with an apical trimetyl phosphite ligand and the Co atom 0.37 Å out of the basal plane. This formal description requires a difference in apical and basal Co-P bonds, contrary to the observations. A difficulty with a model involving a "metallacyclopropene" unit



is also the ambiguity of oxidation states arising from the

⁽¹⁶⁾ Vand, A.; Eiland, P. E.; Pepinsky, R. Acta Crystallogr. 1957, 10, 303.

⁽¹⁷⁾ Moore, F. H. Acta Crystallogr. 1963, 16, 1169.
(18) Cruickshank, D. W. J.; Pilling, D. E.; Bujosa, A.; Lovell, F. M.; Truter, M. R. "Computing Methods and the Phase Problem in X-ray (19) Johnson, C. K. ORTEP, Report ORNL-3794; Oak Ridge National

Laboratory: Oak Ridge, TN, 1970. (20) Davis, B. R.; Payne, N. C.; Ibers, J. A. Inorg. Chem. 1969, 8, 2719.

 ⁽²²⁾ Kirchner, R. M.; Ibers, J. A.; Inorg. Chem. 1974, 13, 1667.
 (23) Stephens, F. S. J. Chem. Soc. A 1970, 2745.

Table I. Final Fractional Coordinates with Estimated Standard Deviations in Parentheses

$\begin{array}{cccccccccccccccccccccccccccccccccccc$	atom	x	У	z
$\begin{array}{llllllllllllllllllllllllllllllllllll$	Со	0,12407 (9)	0.82079 (6)	0.75886 (5)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	P(1)	0.11812 (20)	0.86814(12)	0.63783(11)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	P(2)	0.27838(19)	0.71077(12)	0.77202(11)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	P(3) = O(11)	0.28434(19)	0.90865(12)	0.84979(11)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O(11) O(12)	0.0384 (8)	0.8120(4) 0.8762(4)	0.5509(3)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O(12) O(13)	0.2821(0) 0.0326(7)	0.8702(4) 0.9572(4)	0.0304(3) 0.6012(3)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O(21)	0.2658(5)	0.6506(3)	0.6928(3)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O(22)	0.2707(7)	0.6439 (3)	0.8424(4)
$\begin{array}{ccccccc} O(31) & 0.4059(6) & 0.8743(4) & 0.9397(3) \\ O(32) & 0.3970(6) & 0.9702(4) & 0.8257(4) \\ O(33) & 0.1887(5) & 0.9804(3) & 0.8735(3) \\ C(11) & -0.1210(11) & 0.8034(7) & 0.5095(6) \\ C(12) & 0.3107(11) & 0.9088(7) & 0.5630(6) \\ C(13) & 0.0477(12) & 1.0302(6) & 0.6562(6) \\ C(21) & 0.1214(9) & 0.6098(6) & 0.6406(5) \\ C(22) & 0.3730(13) & 0.5704(6) & 0.8694(7) \\ C(33) & 0.5590(10) & 0.7067(8) & 0.7669(7) \\ C(31) & 0.3666(13) & 0.8158(8) & 0.9924(6) \\ C(32) & 0.5345(9) & 0.9412(6) & 0.8190(6) \\ C(33) & 0.2584(11) & 1.0446(7) & 0.9389(7) \\ O(1) & -0.0543(7) & 0.8836(4) & 0.9166(4) \\ O(2) & -0.1766(6) & 0.8901(4) & 0.7737(3) \\ O(3) & -0.3001(6) & 0.8471(5) & 0.6365(4) \\ \end{array}$	O(23)	0.4565 (6)	0.7312(4)	0.8051 (4)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O(31)	0.4059(6)	0.8743(4)	0.9397 (3)
$\begin{array}{cccccccc} O(33) & 0.1887(6) & 0.9804(3) & 0.8735(3) \\ C(11) & -0.1210(11) & 0.8034(7) & 0.5095(6) \\ C(12) & 0.3107(11) & 0.9088(7) & 0.5630(6) \\ C(13) & 0.0477(12) & 1.0302(6) & 0.6562(6) \\ C(21) & 0.1214(9) & 0.6098(6) & 0.6406(5) \\ C(22) & 0.3730(13) & 0.5704(6) & 0.8694(7) \\ C(23) & 0.5590(10) & 0.7067(8) & 0.7669(7) \\ C(31) & 0.3666(13) & 0.8158(8) & 0.9924(6) \\ C(32) & 0.5345(9) & 0.9412(6) & 0.8190(6) \\ C(33) & 0.2584(11) & 1.0446(7) & 0.9389(7) \\ O(1) & -0.0543(7) & 0.8836(4) & 0.9166(4) \\ O(2) & -0.1766(6) & 0.8901(4) & 0.7737(3) \\ O(3) & -0.3001(6) & 0.8471(5) & 0.6365(4) \\ \end{array}$	O(32)	0.3970 (6)	0.9702(4)	0.8257(4)
$\begin{array}{ccccccc} C(11) & -0.1210 \ (11) & 0.3034 \ (7) & 0.5053 \ (6) \\ C(12) & 0.3107 \ (11) & 0.9088 \ (7) & 0.5630 \ (6) \\ C(13) & 0.0477 \ (12) & 1.0302 \ (6) & 0.6562 \ (6) \\ C(21) & 0.1214 \ (9) & 0.6098 \ (6) & 0.6406 \ (5) \\ C(22) & 0.3730 \ (13) & 0.5704 \ (6) & 0.8694 \ (7) \\ C(23) & 0.5590 \ (10) & 0.7067 \ (8) & 0.7669 \ (7) \\ C(31) & 0.3666 \ (13) & 0.8158 \ (8) & 0.9924 \ (6) \\ C(32) & 0.5345 \ (9) & 0.9412 \ (6) & 0.8190 \ (6) \\ C(33) & 0.2584 \ (11) & 1.0446 \ (7) & 0.9389 \ (7) \\ O(1) & -0.0543 \ (7) & 0.8836 \ (4) & 0.9166 \ (4) \\ O(2) & -0.1766 \ (6) & 0.8901 \ (4) & 0.7737 \ (3) \\ O(3) & -0.3001 \ (6) & 0.8471 \ (5) & 0.6365 \ (4) \\ \end{array}$	O(33)	0.1887(5)	0.9804(3)	0.8735(3)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(12)	-0.1210(11) 0.3107(11)	0.8034(7)	0.5095 (6)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(12)	0.0477(12)	1.0302(6)	0.6562(6)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(21)	0.1214(9)	0.6098 (6)	0.6406 (5)
$\begin{array}{ccccc} C(23) & 0.5590(10) & 0.7067(8) & 0.7669(7) \\ C(31) & 0.3666(13) & 0.8158(8) & 0.9924(6) \\ C(32) & 0.5345(9) & 0.9412(6) & 0.8190(6) \\ C(33) & 0.2584(11) & 1.0446(7) & 0.9389(7) \\ O(1) & -0.0543(7) & 0.8836(4) & 0.9166(4) \\ O(2) & -0.1766(6) & 0.8901(4) & 0.7737(3) \\ O(3) & -0.3001(6) & 0.8471(5) & 0.6365(4) \end{array}$	C(22)	0.3730 (13)	0.5704 (6)	0.8694 (7)
$\begin{array}{ccccc} C(31) & 0.3666 & (13) & 0.8158 & (8) & 0.9924 & (6) \\ C(32) & 0.5345 & (9) & 0.9412 & (6) & 0.8190 & (6) \\ C(33) & 0.2584 & (11) & 1.0446 & (7) & 0.9389 & (7) \\ O(1) & -0.0543 & (7) & 0.8836 & (4) & 0.9166 & (4) \\ O(2) & -0.1766 & (6) & 0.8901 & (4) & 0.7737 & (3) \\ O(3) & -0.3001 & (6) & 0.8471 & (5) & 0.6365 & (4) \\ \end{array}$	C(23)	0.5590 (10)	0.7067 (8)	0.7669 (7)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(31)	0.3666(13)	0.8158 (8)	0.9924 (6)
$\begin{array}{cccc} O(33) & 0.2334 (11) & 1.0446 (7) & 0.3335 (7) \\ O(1) & -0.0543 (7) & 0.8836 (4) & 0.9166 (4) \\ O(2) & -0.1766 (6) & 0.8901 (4) & 0.7737 (3) \\ O(3) & -0.3001 (6) & 0.8471 (5) & 0.6365 (4) \end{array}$	C(32)	0.5345(9) 0.2584(11)	0.9412(6) 1 0446(7)	0.8190(6)
$\begin{array}{cccc} O(2) & -0.1766 \ (6) & 0.8901 \ (4) & 0.7737 \ (3) \\ O(3) & -0.3001 \ (6) & 0.8471 \ (5) & 0.6365 \ (4) \end{array}$	O(1)	-0.0543(7)	0.8836(4)	0.9365(1)
O(3) = -0.3001(6) = 0.8471(5) = 0.6365(4)	O(2)	-0.1766(6)	0.8901(4)	0.7737(3)
	O(3)	-0.3001 (6)	0.8471(5)	0.6365 (4)
C(1) = -0.0684(8) = 0.8524(5) = 0.8493(5)	C(1)	-0.0684(8)	0.8524(5)	0.8493 (5)
C(2) 0.0002 (8) 0.7794 (5) 0.8263 (5)	C(2)	0.0002 (8)	0.7794 (5)	0.8263(5)
C(3) = 0.1964(8) = 0.8324(6) = 0.7045(5) C(4) = 0.0820(8) = 0.7656(5) = 0.7246(5)	C(3)	-0.1964(8)	0.8324(6)	0.7045(5)
H(111) = 0.149 = 0.764 = 0.453	H(111)	-0.0820(8) -0.149	0.7656 (5)	0.7340 (5)
H(112) = -0.172 0.867 0.490	H(112)	-0.172	0.867	0.490
H(113) -0.166 0.775 0.552	H(113)	-0.166	0.775	0.552
H(121) 0.431 0.907 0.577	H(121)	0.431	0.907	0.577
H(122) 0.268 0.974 0.548	H(122)	0.268	0.974	0.548
H(123) 0.251 0.868 0.507	H(123)	0.251	0.868	0.507
H(131) = 0.019 1.084 $0.620H(132) = 0.167$ 1.049 0.687	H(131) H(130)	-0.019	1.084	0.620
H(132) = 0.008 = 1.043 = 0.087 H(133) = 0.008 = 1.013 = 0.706	H(132)	0.008	1.043	0.007
H(211) 0.135 0.571 0.590	H(211)	0.135	0.571	0.590
H(212) 0.035 0.659 0.611	H(212)	0.035	0.659	0.611
H(213) 0.084 0.568 0.680	H(213)	0.084	0.568	0.680
H(221) 0.353 0.533 0.918 0.007	H(221)	0.353	0.533	0.918
H(222) 0.493 0.593 0.897 H(222) 0.261 0.590 0.815	H(222) H(222)	0.493	0.593	0.897
H(223) = 0.501 = 0.525 = 0.515 = 0.5	H(231)	0.672	0.525	0.815
H(232) 0.520 0.734 0.702	H(232)	0.520	0.734	0.702
H(233) 0.562 0.637 0.762	H(233)	0.562	0.637	0.762
H(311) 0.465 0.801 1.050	H(311)	0.465	0.801	1.050
H(312) 0.323 0.756 0.957	H(312)	0.323	0.756	0.957
H(313) = 0.278 = 0.844 = 1.010 H(221) = 0.501 = 0.004 = 0.802	H(313)	0.278	0.844	1.010
H(322) = 0.551 = 0.554 = 0.602 = 0.6	H(322)	0.591	0.994	0.002
H(323) 0.611 0.913 0.879	H(323)	0.611	0.913	0.879
H(331) 0.176 1.087 0.946	H(331)	0.176	1.087	0.946
H(332) 0.342 1.082 0.925	H(332)	0.342	1.082	0.925
H(333) 0.320 1.011 1.001	H(333)	0.320	1.011	1.001
H(2) = 0.097 = 0.742 = 0.870 = 0.064 = 0.715 = 0.695 = 0.064 = 0.715 = 0.695 = 0.0000000000000000000000000000000000	H(2) H(4)	-0.064	0.742	0.870

convention of regarding σ -bonded alkyl groups as carbanions in assigning formal oxidation states. According to this convention, COCA is to be regarded as a Co(II) complex, contrary to XPS results which indicate that assignment of a Co(0) oxidation state is more appropriate.

The geometry of trimethyl phosphite ligands is heavily restricted by the metal binding site and conformations with methyl groups oriented toward the top of the phosphorus pyramid are excluded.²⁴ The asymmetric ligands of COCA exhibit two different "two down and one up" arrangements, which are some of the five distinct conformations usually observed in the solid state. In both cases the point symmetry is C_1 instead of C_3 , C_s , or the experimentally unobserved $C_{3\nu}$. While the conformation of the P(2) ligand is one of the eight most stable forms in the free state, the conformation of the P(1) and P(3) phosphites is energetically unfavorable in the isolated molecule. Minor differences in the conformations around P(1) and P(3) are probably on account of packing requirements.

The mean distances of the P and Co atoms to the phosphite oxygen planes are 0.725 Å (range 0.715–0.735 Å) and 2.880 Å (range 2.865–2.895 Å), respectively. The metal is displaced "off-center" by 0.34 Å on the average in the direction of those carbon atoms (C(12), C(22), andC(33) that are most out of the oxygen plane (1.44 Å on average). With the trivalent phosphorus coordination being pseudotetrahedral, the Co-P-O and O-P-O angles are related, and as usual the mean Co-P-O angle is larger (117.1°) and the O-P-O angle (100.6°) smaller than 109.5 Å. The latter is in good agreement with the standard value $(101.4^{\circ}).^{24}$

Although complexation determines the conformation of the $P(OCH_3)_3$ ligands (defines the torsional angles), average bond lengths and angles in the phosphitic ligands in COCA are not significantly different from those observed in other trimethyl phosphites and also are close to the related orthophosphate esters, gaseous $P(OEt)_3$, and strain-free P_4O_6 , with the crystal structure of $P(OCH_3)_3$ being unknown (Table III). Yet, MNDO calculations²⁴ indicate that complexation affects these parameters slightly, leading to some C-O lengthening.

The P-O bonds of the phosphite ligands (1.595 Å) exhibit double-bond character and are shorter than the P–C bonds in triphenylphosphorous $(1.828 \text{ Å})^{28}$ and dicarbonylnitrosyl(triphenylphosphine)cobalt(0) (1.821 Å)¹² by an amount that cannot be accounted for only by the difference in covalent radii of O (0.66 Å) and C (0.77 Å) atoms. Therefore, the P-O lengths fall short of the theoretical single-bond value of 1.73 Å.²⁹ On the basis of the relation between bond order and P(V)-O bond lengths,³⁰ applicable for P(III) compounds after a slight correction (about 0.05 Å), a π -bond order of about 0.4 is derived for the P-O bonds of COCA.

The mean O-C bond length of 1.443 (12) Å and P-O-C angle of 122.9 (4)° in COCA are in good agreement with the usual values of 1.440 Å and 124.0° in $P(OCH_3)_3$ complexes.²⁴ As in $Ru(CO)_4[P(OCH_3)_3]^{31}$ and other crystal structures with disordered $P(OCH_3)_3$ groups,^{22,32-35} the analysis of COCA suffered because of some disorder in the $O-CH_3$ arms of the phosphite ligands, as reflected in the relatively high-temperature factors for the carbon atoms of the ligands (see supplementary material).

Crystallographic evidence for strong cobalt-maleic anhydride interaction in COCA is given by a considerable conformational change of the MA ring compared to the

(31) Cobbledick, R. E.; Einstein, F. W. B.; Pomeroy, R. K.; Spetch, E.
R. J. Organomet. Chem. 1980, 195, 77.
(32) Drew, M. G. B.; Wilkins, J. D. J. Chem. Soc. Dalton Trans. 1975,

⁽²⁴⁾ Bart, J. C. J.; Favini, G.; Todeschini, R., submitted for publication in Phosphorus Sulfur.

⁽²⁵⁾ Corbridge, D. E. C. "The Structural Chemistry of Phosphorus"; Elsevier: Amsterdam, 1974; p 264. (26) Cruickshank, D. W. J. Acta Crystallogr. 1964, 17, 675.

⁽²⁷⁾ Reference 25; p 201.
(28) Daly, J. J. J. Chem. Soc. 1964, 3799.
(29) Pauling, L. "The Nature of the Chemical Bond"; Cornell University Press: Ithaca, NY, 1960; p 321.
(30) Cruickshank, D. W. J. J. Chem. Soc. 1961, 5486.
(21) Child D. E. Entricking, W. R. Bernster, P. K. Setther, F.

^{1984.}

⁽³³⁾ Love, R. A.; Chin, H. B.; Koetzle, T. F.; Kirtley, S. W.; Whittlesey,
B. R.; Bau, R. J. Am. Chem. Soc. 1976, 98, 4491.
(34) Teller, R. G.; Wilson, R. D.; McMullan, R. K.; Koetzle, T. F.; Bau,
R. J. Am. Chem. Soc. 1978, 100, 3071.

⁽³⁵⁾ Cann, K.; Riley, P. E.; Davis, R. E.; Pettit, R. Inorg. Chem. 1978, 17, 1421.

Table II. Bond Distances (A) and Angles (deg) with Esd's in Parentheses

		Bond Dist	ances		
$\begin{array}{c} \text{Co-P(1)} \\ \text{Co-P(2)} \\ \text{Co-P(3)} \\ \text{Co-C(2)} \\ \text{Co-C(4)} \\ \text{Co-C(4)} \\ \text{Co-C(4)} \\ \text{Co-X}^{b} \\ \text{C(2)=C(4)} \\ \text{O(2)-C(1)} \\ \text{O(2)-C(3)} \\ \text{O-C}^{a} \end{array}$	$\begin{array}{c} 2.153 (2) \\ 2.198 (2) \\ 2.164 (2) \\ 2.172 (2) \\ 2.039 (7) \\ 2.027 (8) \\ 2.033 (7) \\ 1.898 \\ 1.451 (14) \\ 1.413 (13) \\ 1.423 (14) \\ 1.418 (14) \end{array}$	$\begin{array}{c} P(1)-O(11)\\ P(1)-O(12)\\ P(1)-O(13)\\ P(2)-O(21)\\ P(2)-O(22)\\ P(2)-O(23)\\ P(3)-O(31)\\ P(3)-O(32)\\ P(3)-O(33)\\ P-O^a\\ C(1)-C(2)\\ C(3)-C(4)\\ C-C^a\\ \end{array}$	$\begin{array}{c} 1.616\ (6)\\ 1.575\ (6)\\ 1.593\ (7)\\ 1.596\ (5)\\ 1.598\ (7)\\ 1.594\ (7)\\ 1.596\ (8)\\ 1.601\ (6)\\ 1.582\ (5)\\ 1.594\ (6)\\ 1.431\ (10)\\ 1.439\ (13)\\ 1.435\ (13)\\ 2.225\ (11)\ (11)\ (11)\\ 2.225\ (11)\$	$\begin{array}{c} O(11)-C(11)\\ O(12)-C(12)\\ O(13)-C(13)\\ O(21)-C(21)\\ O(22)-C(22)\\ O(23)-C(23)\\ O(31)-C(31)\\ O(32)-C(32)\\ O(33)-C(33)\\ O-C^a\\ O(1)=C(1)\\ O(3)=C(3)\\ O=C^a\\ \end{array}$	$\begin{array}{c} 1.405 \ (14) \\ 1.461 \ (11) \\ 1.432 \ (10) \\ 1.452 \ (12) \\ 1.447 \ (14) \\ 1.417 \ (10) \\ 1.419 \ (13) \\ 1.429 \ (10) \\ 1.437 \ (12) \\ 1.443 \ (12) \\ 1.193 \ (10) \\ 1.207 \ (14) \\ 1.200 \ (12) \end{array}$
		Co…H(2) Co…H(4)	2.337(1) 2.347(1)		
		Bond Ar	ngles		
$\begin{array}{c} \text{Co-P(1)-O(11)} \\ \text{Co-P(1)-O(12)} \\ \text{Co-P(1)-O(13)} \\ \text{Co-P(2)-O(21)} \\ \text{Co-P(2)-O(22)} \\ \text{Co-P(2)-O(23)} \\ \text{Co-P(3)-O(31)} \\ \text{Co-P(3)-O(31)} \\ \text{Co-P(3)-O(33)} \\ \text{Co-P(3)-O(33)} \\ \text{Co-P(-Oa)} \\ \text{Co-C(2)-C(1)} \\ \text{Co-C(2)-C(2)} \\ \text{Co-C(2)-C(2)-C(2)} \\ \text{Co-C(2)-C(2)-C(2)} \\ \text{Co-C(2)-C(2)-C(2)} \\ \text{Co-C(2)-C(2)-C(2)} \\ \text{Co-C(2)-C(2)-C(2)-C(2)} \\ Co-C(2)-C(2)-C(2)-C(2)-C(2)-C(2)-C(2)-C(2)$	$120.7(2) \\112.7(2) \\118.7(3) \\122.6(2) \\110.5(2) \\117.3(2) \\120.9(3) \\123.1(2) \\107.7(2) \\117.1(2) \\109.3(3) \\69.6(4) \\68.6(4) \\107.9(4) \\97.1(4) \\102.1(4) \\98.9(4) \\99.4(4) \\126.9 \\104.3 \\120.9 \\$	$\begin{array}{l} P(1)-Co-C(2)\\ P(1)-Co-C(4)\\ P(2)-Co-C(2)\\ P(2)-Co-C(2)\\ P(3)-Co-C(2)\\ P(3)-Co-C(2)\\ P(3)-Co-C(4)\\ O(11)-P(1)-O(13)\\ O(12)-P(1)-O(13)\\ O(12)-P(1)-O(13)\\ O(21)-P(2)-O(22)\\ O(21)-P(2)-O(23)\\ O(22)-P(2)-O(23)\\ O(31)-P(3)-O(33)\\ O(32)-P(3)-O(33)\\ O(32)-P(3)-O(3)\\ O(32)-P(3)-O(3)\\ O(32)-P(3)-O(3)\\ $	$146.5 (4) \\106.8 (2) \\102.2 (1) \\104.5 (2) \\101.5 (1) \\139.7 (3) \\98.1 (2) \\97.0 (2) \\106.4 (2) \\103.8 (2) \\97.2 (2) \\102.7 (2) \\97.6 (2) \\105.3 (2) \\99.1 (2) \\100.6 (2) \\107.1 (3) \\106.7 (4) \\106.9 (4) \\107.5 (4) \\$	$\begin{array}{c} P(1)-O(11)-C(11)\\ P(1)-O(12)-C(12)\\ P(1)-O(13)-C(13)\\ P(2)-O(21)-C(21)\\ P(2)-O(22)-C(22)\\ P(2)-O(23)-C(23)\\ P(3)-O(31)-C(31)\\ P(3)-O(32)-C(32)\\ P(3)-O(33)-C(33)\\ P(3)-O(33)-C(33)\\ P(3)-O(33)-C(33)\\ P(3)-O(2)\\ O(3)=C(3)-O(2)\\ O(3)=C(3)-O(2)\\ O(3)=C(3)-C(4)\\ O=C-C^a\\ O(2)-C(1)-C(2)\\ O(2)-C(3)-C(4)\\ O-C-C^a\\ \end{array}$	122.1 (5123.9 (4)121.4 (4)120.2 (4)121.3 (5)127.9 (4)122.6 (5)124.1 (4)122.7 (4)122.9 (4)117.7 (3)117.5 (4)117.5 (4)133.2 (4)133.8 (5)133.5 (5)109.0 (4)108.7 (3)108.9 (4)
P-Co-X"	117.4				

^a This is the mean distance or mean angle. ^b X is the midpoint of C=C.

Table III. Geometry around Phosphorous

compound	⟨ P-O ⟩, Å	⟨ O−C ⟩, Å	$\langle O-P-O \rangle$, deg	$\langle P-O-C \rangle$, deg	ref
$[CHC(O)]_2OCo[P(OCH_3)_3]_3$	1.595	1.443	100.6	122.9	this work
$P(OC_2H_5)_3$	1.600	1.42	96	120	25
$P(OCH_3)_3$ complexes	1.583	1.440	101.4	124.0	24
P_4O_6	1.638		100		26
substituted phosphates	1.590	1.44	100	116	27

free anhydride,³⁶ electron delocalization in the ligand and the Co-C(olefin) distance of 2.033 Å. (The distance of cobalt to the maleic anhydride plane is 1.88 Å). The MA ring symmetry changes from C_{2v} in the free anhydride to an idealized C_s configuration in COCA. The deformation results from the two carbonyl groups bending out of the mean plane of the ring away from the metal atom by an average of 0.2 Å (see Figure 4 and Table IV). Similar distortions have previously been observed, e.g., in cyclopentadienyl(duroquinone)cobalt dihydrate.³⁷ Free MA is only slightly nonplanar with the ring oxygen atom 0.03 Å out of the plane of the other atoms.³⁶

In the absence of any significant differences between the chemically equivalent bond data in free MA³⁶ and in various compounds containing maleic anhydride such as COCA, tricarbonyl(2,3-bis(diphenylphosphino)maleic anhydride)cobalt (COCAMB),³⁸ tricarbonyl(2,3-bis(diphenylphosphino)maleic anhydride)iron (FECAMB),³⁸ diiodo(2,3-bis(diphenylphosphino)maleic anhydride)nickel(II) 1,2-dichloroethane solvate (NICAMB),³⁹ 2,3-bis(diphenylstibino)maleic anhydride (STIMA),⁴⁰ and various diadducts,⁴¹⁻⁵⁰ we shall discuss the dimensions of MA in

- (38) Fenske, D. Chem. Ber. 1979, 112, 363.
 (39) Becher, H. J.; Bensmann, W.; Fenske, D. Chem. Ber. 1977, 110, 315
- (40) Fenske, D.; Teichert, H.; Prokscha, H.; Renz, W.; Becher, H. J. (40) Fenske, D.; Teichert, H.; Frokscha, H.; Kenz, W.; Becher, H. J.
 J. Monatsh, Chem. 1980, 111, 177.
 (41) Filippini, G.; Gramaccioli, C. M.; Rovere, C. Simonetta, M. Acta Crystallogr., Sect. B. 1972, B28, 2869.
 (42) Destro, R.; Filippini, G.; Gramaccioli, C. M.; Simonetta, M. Acta Crystallogr., Sect. B 1971, B27, 2023.
 (43) Craig, R. E. R.; Craig, A. C.; Larsen, R. D.; Caughlan, C. N. J. Org. Chem. 1977, 42, 3188.
 (44) Crait A. D. Bracki, E. P. Bin, di Screenerin, L. Teinchedene Letter.

⁽³⁶⁾ Marsh, R. E.; Ubell, E.; Wilcox, H. E.; Acta Crystallogr. 1962, 15, 35.

⁽³⁷⁾ Utchman, V. A.; Dahl, L. F. J. Organomet. Chem. 1972, 40, 403.

⁽⁴⁴⁾ Caglioti, L.; Foresti, E.; Riva di Sanseverino, L. Tetrahedron Lett. 1970, 16, 1347.

Table IV. Planarity of Groups of Atoms in the Structure^a

Plane 1								
0.806x + 0.566y - 0.173z - 0.131 = 0								
O(2) C(2) C(4)	0.057 (6) 0.024 (8) 0.011 (8)	C(1) C(3)	-0.050 (8) -0.042 (9)					
Not Defining the Plane								
Co O(3) P(2)	1.879 (1) -0.162 (7) 1.996 (2)	O(1) P(1) P(3)	-0.211 (7) 3.221 (2) 3.144 (2)					
Plane 2								
0.980x + 0.182y - 0.085z + 1.470 = 0								
P(1) P(3)	0.000 (2) 0.000 (2)	P(2)	0.000 (2)					
Not Defining the Plane								
Co C(4)	-1.027 (1) -2.913 (8)	C(2)	-2.827 (8)					

Dihedral Angles between Planes: Plane 1-Plane 2 = 24.9°

^a Equations of the least-squares planes are expressed in a*bc orthogonal space as Px + Qy + Rz - S = 0. The distances of the atoms from the planes are in A.

these compounds in terms of the average of the observed values (Table V). The C=C distance in COCA (1.451 Å) is significantly larger than that of 1.303 Å in MA,³⁶ 1.325-1.386 Å in several metal complexes, and 1.33 Å in ethylene.⁵¹ which is usually chosen as the normal C = Cbond, and indicates a weakening of the double bond. Yet, the bond is considerably stronger than the observed single bonds in several diadducts (Table V). The mean C-C bond distance in COCA is among the shortest and is significantly less than the value of 1.470 Å in free MA,³⁶ indicating a considerable degree of π -double-bond character. Further evidence for the greater double-bond character of the C(1)-C(2) and C(3)-C(4) bonds in COCA compared to free MA^{36} is given by the external bond angles at C(1) and C(3): the O=C-O angles are 16° smaller than the O=C-Cangles as compared to 11° in free MA. The mean C-O bond length within the ring of COCA (1.418 Å) is longer than in MA (1.388 Å) and is an extreme value. The mean C=O bond (1.200 Å) is slightly longer than in the free ligand (1.189 Å). The changes in the bond angles are less pronounced than in case of the diadducts. The variations in the dimensions of the ring of COCA as compared to MA and the other complexes indicate strong electron delocalization which is achieved even though cobalt is located sideways with respect to the ligand (Figure 3) and is not at all involved in any short contacts to the C=O part. The out-of-plane tipping of the carbonyl oxygen atoms (Figure

(45) Craig, R. E. R.; Craig, A. C.; Larsen, R. D.; Caughlan, C. N. J. Org. Chem. 1976, 41, 2129.

- (47) Cameron, A. F.; Ferguson, G. J. Chem. Soc. B 1970, 943.
 (48) Destro, R.; Filippini, G.; Gramaccioli, C. M.; Simonetta, M. Acta Crystallogr., Sect. B 1969, B25, 2465.
- (49) Filippini, G.; Induni, G.; Simonetta, M. Acta Crystallogr. Sect. B 1973, B29, 2471.
- (50) Murray-Rust, P.; Murray-Rust, J. Acta Crystallogr., Sect. B 1977, B33, 3929.
- (51) Bartell, L. S.; Bonham, R. A. J. Chem. Phys. 1957, 27, 1414. (52) Otsuka, S.; Yoshida, T.; Tatsuno, Y. J. Am. Chem. Soc. 1971, 93, 6462
- (53) Tolman, C. A.; Seidel, W. C. J. Am. Chem. Soc. 1974, 96, 2774.
 (54) Yamamoto, T.; Yamamoto, A.; Ikeda, S. J. Am. Chem. Soc. 1971, 93. 3350.
- (55) Weiss, E.; Stark, K.; Lancaster, J. E.; Murdoch, H. D. Helv. Chim. Acta 1963, 46, 288.
- (56) Weiss, E.; Stark, K. Z. Naturforsch., Sect. B: Anorg. Chem., Org Chem., Biochem., Biophys. Biol. 1965, 20B, 490.
- (57) Cenini, S.; Ugo, R.; Monica, G. L. J. Chem. Soc. A 1971, 409.

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ی د ک د د	rei	36 this morb	28 28		55	40	38	41-50	eic anhydride)iro. tricarbonyl(2,3-
,0000	232	107.5 (10)	(+) 0.1 UT			108.9 ()		110.3 (6)	phosphino)male de: COCAMB, 1
5	123	107.7 (10)	100.9 (4)			(···) £'./.01		110.4(6)	3-bis(diphenyl _i) maleic anhydri
	324	120.7 (10)	(4) 0.711			120.9 ()		119.6(6)	3, tricarbonyl(2 diphenvlstibino
	124	131.6(10)	133.5 (5)			131.8()		129.9(6)	alt(0); FECAMI te: STIMA, bis(
	1'12	108.5(10)	106.9 (4)			108.2()		104.3(6)	: anhydride)cob oroethane solva
	23	1.388 (5)	1.418(11)	1.395(5)	1.40(1)	1.402(8)	1.417(5)	1.385 (6)	1 0-2 1 1 0-2 1 1 0-2 1 1 1 1 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2
	24	1.189(5)	1.200(12)	1.185(5)	1.17(1)	1.185(8)	1.209(5)	1.193(6)	tris(trimethyl pl c subvdride)nic
	12	1.470 (5)	1.435(11)	1.497(5)	1.50(1)	1.504(8)	1.435(5)	1.502(6)	tydride; COCA,
	11′	1.303 (5)	1.451(14)	1.325(4)	1.33(1)	1.338(8)	1.386(5)	1.528(6)	MA, maleic anh
	compd ^a	MA	COCA	FECAMB	NICAMB	STIMA	COCAMB	diadducts	^a Abbreviations:

Table V. Comparison of Mean Bond Distances (A) and Angles (deg) in Maleic Anhydride and Its Adducts

1 1

⁽⁴⁶⁾ Baggio, S.; Barriola, A.; de Perazzo, P. K. J. Chem. Soc., Perkin

•			
compd	ν (C=O), cm ⁻¹	ref	
MA	1850, 1780	this	
	(Nujol mull)	work	
$(MA)Co(P(OCH_3)_3)$	1787, 1722	this	
	(Nujol mull)	work	
$(MA)Pd(t-BuNC)_{a}$	1805,1732	52	
	(Nujol mull)		
(MA)Ni(t-BuNC)	1799.1730	52	
	(Nujol mull)		
$(MA)Ni[P(O-o-tolvl)_{a}]_{a}$	1805, 1733 (CH.Cl.)	53	
MA	1845, 1777 (CH.Cl.)	53	
(MA), Ni(bpy)	1815, 1730 (KBr)	54	
(MA)Fe(CO).	1824, 1746 (KBr)	55	
(MA).Ni	1810, 1730 (KBr)	56	
(MA)Pt[PPh]	1800, 1725 (CHCL)	57	
MA	1850 1770 (CHCL)	57	
*****	10000, 10000000000000000000000000000000	•••	

^a Abbreviation: MA, maleic anhydride. The table indicates that the frequency in an olefin-bonded MA complex is lower than in free MA and decreases as the back-donation from the metal increases.

4) is likely to be the result of an effect that is essentially electronic in origin. The extensive degree of electron delocalization, which causes the major bond length variations, probably leads to this distortion.

Stabilization of the complex is accomplished in part by an electron transfer from the metal to give aromatic character. The bonding between cobalt and maleic anhydride arises primarily from interactions between the highest occupied molecular orbital (HOMO) of the olefin and the lowest unoccupied molecular orbital (LUMO) of $Co[P(OCH_3)_3]_3$ and between the HOMO of the Co[P(OC- $H_{3}_{3}_{3}_{3}$ and π^{*} LUMO of maleic anhydride. The former interaction can be considered as the donation of olefin π electrons to the metal and the latter as the back-donation from a d orbital of the metal to the olefin π^* orbital. The effect is confirmed indirectly by the relatively small decrease of the C=O stretching frequencies from 1780 and 1850 cm⁻¹ in free MA to 1722 and 1787 cm⁻¹ in COCA. Similar features of lower C=O stretching frequencies in complexes compared to free MA have been observed before (see Table VI). There exists an approximate linear relationship between $\nu(C=0)$ and the electron affinity of the unsaturated ligand.^{58,59} Infrared spectral evidence thus confirms that the C=O groups are not directly involved in π coordination in COCA as otherwise the shifts in ν -(C=O) would be much higher.^{60,61} This is also in accordance with the greater mean distance of Co-C(O) of 2.838 Å as compared to Co-X of 1.898 Å (X is midpoint Organometallics, Vol. 2, No. 5, 1983 633

of C=C). This differs greatly from cyclopentadienyl(duroquinone)cobalt dihydrate,³⁷ where the metal is symmetrically located with respect to the ligand and interacts with the π orbitals of the carbonyl groups. In this compound Co-X and Co-C(O) bond distances are 1.984 and 2.370 Å; the carbonyl bond is stretched to 1.282 Å.

The bonding properties of many previously synthesized MA complexes (see Table VI) are probably similar to those observed in COCA. In the complexes of $Pd(0)^{52}$ and $Pt(0)^{57}$ we notice $\nu(C=0)$ shifts of ca. 50 cm⁻¹ as compared to about 60 cm⁻¹ in COCA. It is then reasonable to suppose that the carbonyl group is again only indirectly involved in bonding to these metals.

Cenini et al.⁵⁷ have suggested that the reduction of ν -(C=O) of olefins with conjugated carbonyl groups provides a measure of metal-olefin π bonding. The electronic effect of the C=O substituents of the metal-olefin geometry is consistent with the $\sigma-\pi$ formalism^{62,63} for metal-olefin bonding. In this interpretation, the C=O group lowers the olefin π^* orbital energy promoting $d\pi - \pi^*$ donation from the cobalt atom. Increased population of the π^* olefin orbital decreases the C=C bond order and usually leads to a shift of about 150 cm⁻¹ to 1450-1500 cm⁻¹ of the infrared band related to the double bond. This band was not clearly identified in COCA (assignment was difficult due to the presence of other bands). However, the change in the double bond character in the olefin is expressed indirectly by the shift of the $\nu(C==0)$ bands, as occurs also in other complexes such as MAFe(CO)455 and [Pt-(PPh₃)₂MA].⁵⁷

Electron-withdrawing olefins such as MA (with an high Alfrey-Price e value⁶⁴) give complexes with correspondingly higher frequencies of the charge-transfer bands, and hence the lowering of the d orbital energy levels is indicated. In case of MA, back-donation causes considerable charge transfer accompanied by oxidation of cobalt and the resulting complex becomes paramagnetic. Therefore, we consider cobalt in COCA to be only formally zero valent. Electron-withdrawing substituents such as C=O on the olefin stabilize the π bond formed by the latter with the zero-valent metal.

A survey of the short intermolecular contacts in the structure (Co-H(2) = 2.337 (1) Å and Co-H(4) = 2.347 (1) Å) indicates that they conform to normal Van der Waals interactions.

Registry No. I (R = Et), 63372-41-8; III, 82555-94-0.

Supplementary Material Available: A table of anisotropic thermal parameters and a listing of structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

⁽⁵⁸⁾ Scott, R. N.; Shriver, D. F.; Vaska, L. J. Am. Chem. Soc. 1968, 90, 1079.

⁽⁵⁹⁾ Baddley, W. H. J. Am. Chem. Soc. 1968, 90, 3705.

 ⁽⁶⁰⁾ Fritz, H. P.; Schrauzer, G. N. Chem. Ber. 1961, 94, 650.
 (61) King, R. B.; Fronzaglia, A. Inorg. Chem. 1966, 5, 1837.

⁽⁶²⁾ Dewar, M. J. S. Bull. Soc. Chim. Fr. 1951, 18, C79.

⁽⁶³⁾ Chatt, J.; Duncanson, L. A. J. Chem. Soc. 1953, 2939.

⁽⁶⁴⁾ Brandrup, J.; Immergut, E. H. "Polymer Handbook"; Interscience: New York, 1966; Vol. II, p 341.