Journal of Organometallic Chemistry, 252 (1983) 221–229
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF THE ELECTRON RICH COMPLEXES $Co(\eta\text{-}C_5Me_5)(R_2PCH_2CH_2PR_2)$ (R = Me, Ph); PHOTOELECTRON SPECTROSCOPIC STUDIES OF SOME PENTAMETHYLCYCLOPENTADIENYLPHOSPHINECOBALT COMPLEXES

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(Received February 25th, 1983)

Summary

The compounds $Co(\eta\text{-}C_5Me_5)(R_2PCH_2CH_2PR_2)$, (R = Me, Ph) have been prepared and characterized. X-Ray diffraction studies of $Co(\eta\text{-}C_5Me_5)(Me_2PCH_2CH_2PMe_2)$ show the two phosphorus atoms and the ring centroid to have a trigonal coordination around the cobalt. Photoelectron spectral studies show $Co(\eta^5\text{-}C_5Me_5)(R_2PCH_2CH_2PR_2)$ to have rather low first ionization energies of around 5.1 eV, indicating that the metal centre has a very electron rich nature.

Introduction

In the course of a study of pentamethylcyclopentadienylcobalt chemistry, we have noted that previous attempts to synthesise pentamethylcyclopentadienylphosphinecobalt complexes with no other stabilizing ligands [1–5] had failed to produce isolable compounds. However, a recent publication by Werner et al. [6], on the synthesis and basic properties of $Co(\eta\text{-}C_5Me_5)(PMe_3)_2$, prompt us to report the synthesis and structural characterization of the related bidentate phosphine systems $Co(\eta\text{-}C_5Me_5)(R_2PCH_2CH_2PR_2)$, (I, R = Me, II, R = Ph). Werner et al. [6–8] have examined the basicity of d^8 complexes of the general formula $Co(\eta\text{-}C_5R_5)L_2$, where R = H or Me and L = CO or phosphine, and found that the readiness to protonate is a function of ligand. We have carried out a photoelectron study on these compounds in order to investigate how their first ionization energies vary.

Experimental

All compounds were handled under dry nitrogen using standard Schlenk techniques. Photolyses were performed in a water-cooled Pyrex apparatus under a flow of dry nitrogen using a 500 W high-pressure mercury UV lamp. Infrared spectra

0022-328X/83/$03.00

were obtained using on a Perkin–Elmer SP 2000 spectrophotometer. PMR spectra were obtained using a Bruker WH300MHz FT spectrometer. Mass spectra were obtained on a VG Analytical ZAB-1F spectrometer. Elemental analyses were performed in this laboratory: this neccessitated the compounds being handled for a short while in air which led to low results for the samples of Co(η-C_5Me_5)($Me_2PCH_2CH_2PMe_2$).

Co(η-C_5Me_5)$(CO)_2$ (IV) was prepared according to the method of Cotton et al. [9]. Co(η-C_5Me_5)(CO)(PMe_3) (III) was prepared according to the method of Werner et al. [6].

Preparation of [Co(η-C_5Me_5)CO]$_2$

Co(η-C_5Me_5)$(CO)_2$ was heated in a Schlenk tube to about 200°C under static vacuum with a hot air blower. The tube was cooled to room temperature to prevent Co(η-C_5Me_5)$(CO)_2$ subliming, and the CO evolved from the red melt was removed under dynamic vacuum. This was repeated until conversion to the solid, purple [Co(η-C_5Me_5)CO]$_2$ appeared to be complete. Any remaining traces of Co(η-C_5Me_5)$(CO)_2$ were removed by sublimation onto a cold finger at reduced pressure. The product was purified by recrystallization from 40/60 petroleum ether.

Preparation of Co(η-C_5Me_5)($Me_2PCH_2CH_2PMe_2$) (I)

[Co(η-C_5Me_5)CO]$_2$ (0.52 g, 1.17 mmol) and $Me_2PCH_2CH_2PMe_2$ (0.80 g, 5.33 mmol) were dissolved in 40/60 petroleum ether (150 ml) and photolyzed for 22 h. The solvent was removed under reduced pressure to give red, air-sensitive crystals of Co(η-C_5Me_5)($Me_2PCH_2CH_2PMe_2$). Oily impurities were removed at room temperature by a liquid nitrogen cooled probe held in the Schlenk tube under reduced pressure. The compound was sublimed (80°C, 10^{-2} Torr) and recrystallized from 40/60 petroleum ether. (Yield 0.58 g, 72%.)

Elemental analysis: Found: C, 52.8; H, 8.9; Co, 17.03; $C_{16}H_{31}P_2Co$ calcd.: C, 55.81; H, 9.01; Co, 17.15%. PMR (in C_6D_6): δ 1.98, singlet, (η-C_5Me_5); 1.16 δ, averaged multiplet, ($Me_2PCH_2CH_2PMe_2$). IR (Nujol mull, CsI plates): 1415m, 1275w, 1266s, 1233vw, 1158vw, 1024m, 934vs, 920vs, 882vs, 824s, 792w, 698s, 688vs, 654s, 633m, 460m, 396m, 362w, 323w. Mass spectrum: field desorption spectrum showed a parent ion peak at $m/e = 344$.

Preparation of Co(η-C_5Me_5)($Ph_2PCH_2CH_2PPh_2$) (II)

[Co(η-C_5Me_5)CO]$_2$ (0.70 g, 1.58 mmol) and $Ph_2PCH_2CH_2PPh_2$ (0.72 g, 1.81 mmol) in toluene (150 ml) were photolyzed for 17 h. The solvent was removed under reduced pressure and the red-brown solid was extracted with 40/60 petroleum ether. The extract was chromatographed on a 50 cm alumina column under nitrogen. Elution with toluene/petroleum ether (40/60) (1/1) left the compound on the column as a bright yellow band. Elution with diethyl ether removed the product as a deep red band. The solvent was removed under reduced pressure and Co(η-C_5Me_5)($Ph_2PCH_2CH_2PPh_2$) was recrystallized from 40/60 petroleum ether, yielding dark red-brown air-sensitive crystals. (Yield 1.5 g, 85%.)

Elemental analysis: Found: C, 72.38; H, 7.17; Co, 9.43. $C_{36}H_{39}P_2Co$ calcd.: C, 72.97; H, 6.59; Co, 9.97%. PMR (in C_6D_6) δ 1.59, singlet, (η-C_5Me_5); δ 1.76, doublet, J(P–H) 15.8 Hz, ($Ph_2PCH_2CH_2PPh_2$) methylene protons; δ 7.07–7.21 complex multiplet and δ 7.73–7.78, complex multiplet, ($Ph_2PCH_2CH_2PPh_2$) phenyl protons. IR (Nujol mull, CsI plates): 1435s, 1303w, 1175w, 1157vw, 1086m, 1064m, 1046m, 1027m, 997vw, 879w, 820m, 751s, 742s, 699vs, 681s, 534vs, 498s, 492s, 478s, 451s, 444s, 346m, 336m.

Structure determination and refinement

A crystal of I was mounted under Ar in a glass capillary. Data were collected with an Enraf-Nonius CAD4 diffractometer using ω-2θ scans. A total of 4267 unique reflections were collected up to a 2θ value of 54°. An absorption correction was deemed to be unnecessary. Lorenz and polarisation corrections were carried out in the usual manner. Merging equivalent reflections and applying an $I > 3\sigma(I)$ cutoff gave 1146 independent reflections which were used in the structure solution and refinement [10a]. The cobalt position was located using a Patterson map, and subsequent Fourier syntheses yielded all the remaining non-hydrogen atoms which were then refined anisotropically using a large-block approximation. The geometry of the pentamethylcyclopentadienyl ring appeared to be unusually distorted and "soft constraints" were applied to regularise the ring. Although hydrogen atoms could not be located in difference Fourier maps, their inclusion in geometrically calculated positions improved the R-value at convergence from 4.05 to 3.47. The final refinement of 163 parameters gave $R = 3.47$ and $R_w = 4.20$ (a three-term Chebychev weighting scheme was used during the final stages of refinement [10b]). Tables of observed and calculated structure factors may be obtained from the authors.

Photoelectron spectral studies have been carried out using two instruments; a Perkin–Elmer PS16/18 and a PES Laboratories Model 0078. All compounds were investigated using both He(I) and He(II) radiation. Conditions of measurement are noted in Table 4. Intensity measurements are based on data collected by a multiple scan technique, with data stored in a 380Z microprocessor, in order to avoid variations in intensity, which might arise owing to fluctuations in sample pressure over a long time period.

Results

Photolysis of the dimer $[Co(\eta\text{-}C_5Me_5)(\mu\text{-}CO)]_2$ in the presence of either bisdimethylphosphinoethane or bisdiphenylphosphinoethane in petroleum ether or toluene solution resulted in the formation of I and II respectively. The compounds, which are air sensitive dark red crystals, have been characterized by elemental analysis, NMR and IR. The driving force of the photolysis reaction is evidently the chelation by the bidentate phosphine, as the reaction proceeds smoothly, even with considerable crowding as must be experienced in the case of II. In contrast, photolysis of a mixture of $Co_2(\eta\text{-}C_5Me_5)_2(CO)_2$ and PMe_3 led neither to the complex $Co(\eta\text{-}C_5Me_5)(PMe_3)_2$ nor to III, only starting material being isolated after 48 h.

Crystal data. $C_{16}H_{31}P_2Co$ mol.wt. 344.34; space group *Pcmn* (non-standard setting for *Pnma*), *a* 9.095(2), *b* 12.729(3), *c* 16.330(4) Å, *U* 1890.6 Å^3, $Z = 4$, D_c 1.21 g cm^{-1}, μ(Mo-K_α) 0.16 cm^{-1}. Associated data is given in Tables 1–3.

PE data. He(I) and He(II) photoelectron spectra were recorded for $Co(\eta\text{-}C_5Me_5)(CO)_2$, $Co(\eta\text{-}C_5Me_5)(R_2PCH_2CH_2PR_2)$, (R = Me, Ph) and $Co(\eta\text{-}C_5Me_5)(CO)(PMe_3)$. Ionization energies and intensity data are given in Table 4, together with values for $Co(\eta\text{-}C_5H_5)(CO)_2$ [11] for comparative purposes. The He(I)

TABLE 1

FRACTIONAL ATOMIC COORDINATES OF I

Atom	x/a	y/b	z/c	U_{iso}
Co(1)	0.14021(7)	0.2500	−0.07082(4)	0.0450
P(1)	−0.0520(2)	0.2500	−0.00168(9)	0.0650
P(2)	0.2547(2)	0.2500	0.03999(8)	0.0604
C(1)	−0.168(1)	0.1238(9)	−0.0119(9)	0.0814
C(2)	−0.195(1)	0.341(1)	−0.0073(8)	0.0893
C(3)	−0.0117(8)	0.2687(9)	0.1090(4)	0.0696
C(4)	0.1306(9)	0.2061(7)	0.1247(4)	0.0704
C(5)	0.398(1)	0.141(1)	0.0574(7)	0.0894
C(6)	0.350(1)	0.358(1)	0.0779(6)	0.0964
C(11)	0.1213(9)	0.3313(7)	−0.1775(7)	0.0732
C(12)	0.2705(8)	0.3175(5)	−0.1610(5)	0.0559
C(13)	0.2983(6)	0.2088(5)	−0.1549(5)	0.0550
C(14)	0.1714(6)	0.1555(5)	−0.1771(5)	0.0466
C(15)	0.0592(6)	0.2304(7)	−0.1883(4)	0.0666
C(21)	0.049(2)	0.434(1)	−0.1942(7)	0.1243
C(22)	0.383(2)	0.4014(9)	−0.1515(8)	0.1205
C(23)	0.4459(9)	0.160(1)	−0.1460(6)	0.0912
C(24)	0.158(1)	0.0397(7)	−0.1875(7)	0.0968
C(25)	−0.0929(8)	0.208(1)	−0.2167(5)	0.1038

spectra of I, III and IV are shown in Fig. 2. The first three bands, a–c, were too closely spaced for reliable intensity data to be obtained for their separate areas. This was also case for bands d and cp in the spectra of III. For IV, band d was not apparent but the intensity data (Table 4) and the ionization energy trends (Table 4

TABLE 2

THERMAL PARAMETERS FOR I

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Co(1)	0.0461(4)	0.0609(4)	0.0324(3)	0.0000	−0.0007(3)	0.0000
P(1)	0.0457(7)	0.114(1)	0.0532(8)	0.0000	0.0039(7)	0.0000
P(2)	0.0519(8)	0.108(1)	0.0401(7)	0.0000	−0.0070(6)	0.0000
C(1)	0.048(5)	0.092(8)	0.13(1)	−0.001(7)	0.018(6)	−0.002(5)
C(2)	0.060(5)	0.13(1)	0.090(9)	0.007(7)	0.009(6)	0.001(7)
C(3)	0.077(4)	0.099(8)	0.052(3)	−0.002(5)	0.022(3)	0.013(6)
C(4)	0.081(5)	0.119(8)	0.038(3)	0.011(4)	0.001(4)	−0.008(5)
C(5)	0.068(6)	0.17(2)	0.077(7)	0.030(8)	−0.015(6)	0.024(7)
C(6)	0.13(1)	0.12(1)	0.067(6)	0.007(7)	−0.027(8)	−0.037(8)
C(11)	0.14(1)	0.11(1)	0.038(6)	0.018(7)	0.005(5)	0.060(9)
C(12)	0.117(9)	0.057(6)	0.033(5)	0.009(4)	0.010(6)	−0.026(7)
C(13)	0.047(4)	0.077(7)	0.047(5)	−0.008(4)	−0.000(4)	−0.005(4)
C(14)	0.061(6)	0.047(7)	0.036(6)	−0.002(5)	0.007(4)	−0.007(4)
C(15)	0.059(4)	0.17(1)	0.035(3)	−0.021(7)	−0.012(3)	0.014(8)
C(21)	0.43(4)	0.20(2)	0.053(7)	0.013(9)	−0.01(1)	0.21(2)
C(22)	0.31(2)	0.16(1)	0.084(9)	−0.011(8)	0.06(1)	−0.15(2)
C(23)	0.066(5)	0.27(2)	0.056(6)	−0.033(8)	0.001(5)	0.051(9)
C(24)	0.22(2)	0.069(6)	0.069(7)	−0.014(6)	0.021(8)	−0.030(9)
C(25)	0.075(5)	0.37(4)	0.059(5)	−0.06(1)	−0.025(4)	0.03(1)

TABLE 3

SELECTED BOND DISTANCES (Å) AND ANGLES (°)

Co–C(11)	2.033(10)	P(1)–Co–P(2)	87.05(6)
Co–C(13)	2.055(7)	Co–P(1)–C(3)	111.19(23)
Co–C(15)	2.070(5)	Co–P(1)–C(2)	126.83(38)
Co–C(12)	2.076(8)	Co–P(1)–C(1)	114.42(32)
Co–P(1)	2.081(2)	Co–P(2)–C(4)	109.87(25)
Co–P(2)	2.088(1)	Co–P(2)–C(6)	123.78(41)
Co–C(14)	2.130(8)	Co–P(2)–C(5)	117.71(39)
		P(1)–C(3)–C(4)	105.15(50)
P(1)–C(2)	1.741(13)	P(2)–C(4)–C(3)	103.26(48)
P(1)–C(3)	1.859(7)	C(15)–C(11)–C(12)	107.33(59)
P(1)–C(1)	1.930(12)	C(11)–C(12)–C(13)	108.16(61)
		C(12)–C(13)–C(14)	108.21(59)
P(2)–C(6)	1.740(13)	C(13)–C(14)–C(15)	107.79(47)
P(2)–C(4)	1.870(7)	C(14)–C(15)–C(11)	108.05(48)
P(2)–C(5)	1.927(13)		
C(3)–C(4)	1.540(11)		
C(11)–C(12)	1.395(7)		
C(12)–C(13)	1.410(6)		
C(13)–C(14)	1.387(6)		
C(14)–C(15)	1.408(7)		
C(15)–C(11)	1.414(8)		
C(11)–C(21)	1.489(8)		
C(12)–C(22)	1.487(8)		
C(13)–C(23)	1.487(7)		
C(14)–C(24)	1.489(8)		
C(15)–C(25)	1.487(7)		

TABLE 4

VERTICAL IONIZATION ENERGIES, BAND INTENSITIES AND MEASUREMENT CONDITIONS FOR THE PE SPECTRA OF $Co(\eta\text{-}C_5Me_5)L_2$, WHERE $L_2 = Me_2PCH_2CH_2PMe_2$, I; $Ph_2PCH_2CH_2PPh_2$, II; $(CO)(PMe_3)$, III; $(CO)_2$, IV AND $Co(\eta\text{-}C_5H_5)(CO)_2$, V [11]

Vertical ionization energies (eV)								Measurement conditions
Band	a	b	c	d	cp	p or Ph	Other main bands	Intensity [a], temperature
I	5.16	5.58	5.96	6.77	7.66	9.02, 9.49	10.92, 13.53, 15.96	1000 c/s, 94°C
II	5.17	5.51	5.85	6.65	7.40	8.44, 8.85	10.53, 11.55, 13.73	4000 c/s, 200°C
III	5.99	6.35	6.88	7.75	8.02	9.63	10.91, 13.33	1000 c/s, 75°C
IV	6.93	7.29	7.89		8.84		11.22, 13.56, 16.71	400 c/s, 51°C
V	7.51	7.78	8.65	9.17	9.90		13.52	

Percentage distribution of intensity among bands; a + b + c/d + cp

	He(I)		He(II)	
	a + b + c	d + cp	a + b + c	d + cp
I	43	57	50	50
II	41	59	43	57
III	43	57	47	53
IV	40	60	48	52

[a] c/s = counts sec^{-1}.

and Fig. 2) strongly suggest that it lies under the cp band. The intensity data recorded in Table 1 are for the combined intensity of a + b + c relative to d + cp. Their intensity ratio, (a + b + c)/(d + cp), shows an increase on changing the photon energy from He(I) to He(II). Where it can be ascertained this increase is due to a relative decrease in intensity of the cp band at higher photon energies which supports an assignment to ionization of the cyclopentadienyl e_1 electrons. The band profile suggests that band a undergoes a decrease in relative intensity in all He(II) spectra when compared with bands b and c. Though it is of comparable height to band b in the He(I) spectra, its maximum is ca. 75% lower in the He(II) spectra.

Discussion

To our knowledge I is the first bisdimethylphosphinoethanecobalt complex to be characterised crystallographically. Figure 1 represents a SNOOPI [12] drawing of I. The cobalt and phosphorus atoms lie in a crystallographic mirror plane inclined at 91° with respect to the least-squares best plane through the pentamethylcyclopentadienyl ring. The ring is disordered with respect to the mirror plane as are the carbon atoms of the bisdimethylphosphinoethane ligand and this disorder together with the small number of observed reflections has limited the overall quality of the crystal structure. The coordination around cobalt in the complex is very similar to that in $Co(\eta\text{-}C_5Me_5)(CO)_2$ (IV) [13] as the following three comparisons make clear. The Co ring-centroid distances in I and IV are 1.695 and 1.703 Å respectively. The "bite-angle" of bisdimethylphosphinoethane in I is 87.05(6)° compared to 93.7° for the two carbonyl ligands in IV. Unfortunately, due to the presence of disorder, it was not possible to identify any distortions in the pentamethylcyclopentadienyl ring of the kind identified by Dahl in IV. The methyl groups on the ring were bent out of the plane of the ring away from the cobalt atom by an average 0.13 Å compared with 0.088 Å in IV. The Co–P bond lengths were 2.081(2) and 2.088(1) Å, slightly shorter than those observed in $Co(diphos)(NO)_2^+$ (average 2.246 Å) [14].

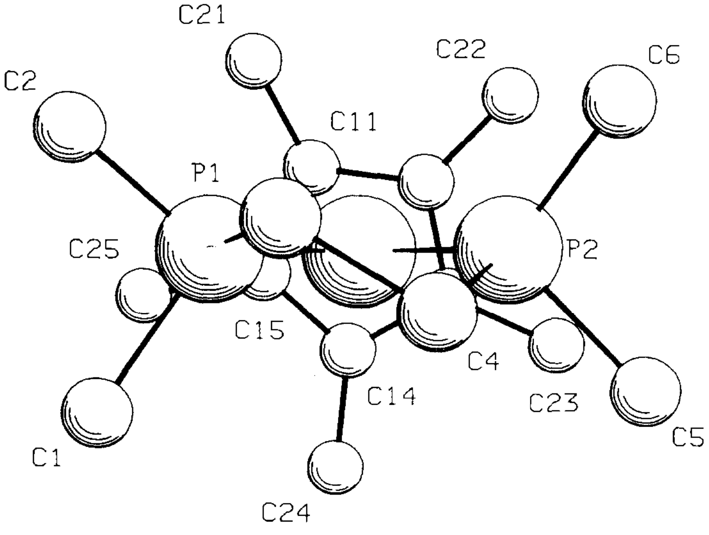

Fig. 1. SNOOPI drawing of $Co(\eta\text{-}C_5Me_5)(Me_2PCH_2CH_2PMe_2)$.

The photoelectron spectra of the compounds $Co(\eta\text{-}C_5Me_5)L_2$ show a progressive decrease in first ionization energy as carbon monoxide is substituted by phosphine. This is illustrated in Fig. 2. Permethylation of the ring also results in easier ionization of such compounds than of their unsubstituted cyclopentadienyl analogues [11]. The combination of both of these factors results in an extremely low first ionization energy for $Co(\eta\text{-}C_5Me_5)(Me_2PCH_2CH_2PMe_2)$ of 5.16 eV. The only other cobalt compounds with ionization energies in this range are the 19 electron metallocenes [15].

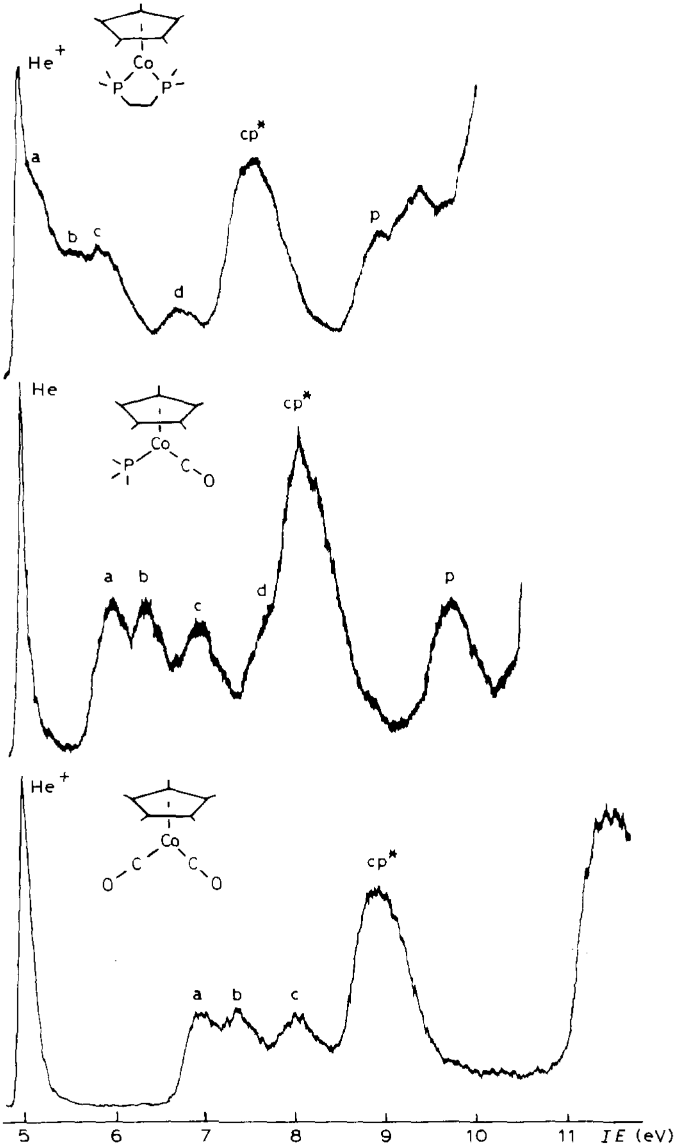

Fig. 2. He(I) photoelectron spectra of $Co(\eta\text{-}C_5Me_5)L_2$, where $L_2 = (CO)_2$, $(CO)(PMe_3)$, $Me_2PCH_2CH_2PMe_2$. The He self-ionization band is also included in the trace as a reference point.

The electronic structure of $Co(\eta\text{-}C_5H_5)(CO)_2$ [16] and related compounds [17] have been the subject of several theoretical treatments, mainly by extended Hückel methods; we will summarize these results here in a qualitative manner. It is fruitful to use two approaches: to consider the binding of a metal cyclopentadienyl moiety to two carbonyl ligands or to look at the binding of a cyclopentadienyl ring to a bent $M(CO)_2$ unit [18]. Both approaches predict the eight d electrons to occupy orbitals of symmetry a_2, b_1 and $2 \times a_1$. The choice of axes is indicated in Fig. 3. This figure shows that the neutral $M(\eta\text{-}C_5H_5)$ unit has two electrons occupying antibonding orbitals. Binding of this fragment to two π-acceptor carbonyl groups stabilizes the b_1 orbital, two electrons occupy it and are delocalized onto the π-antibonding orbitals of the carbonyl ligands. The orbitals a_2 and $1a_1$ (d_{z^2}) also acquire some π-CO character. As the phosphine ligands are inferior π-acceptors to and better σ-donors than the carbonyl groups, their presence leads to a destabilization of all these orbitals and a lowering of ionization energy. However, calculations on $Pt(PH_3)_2$ [19] have shown that a similar orbital ordering should exist for a MP_2 unit.

The approach illustrated on the right hand side of Fig. 2, in which a bent $M(CO)_2$ unit [18] is combined with a cyclopentadienyl ring, emphasizes the stabilization of the a_2, b_1, and $1a_1$ d orbitals by back donation to the two CO ligands, and the destabilization of the b_2 orbital resulting from its MCO σ-antibonding character.

The differential interaction of the metal b_1 and b_2 orbitals with the ligand e_1 orbitals has been emphasized by Dahl et al. [13] in their careful examination of the crystal structure of $Co(\eta\text{-}C_5Me_5)(CO)_2$. They observed a distortion of the ring consistent with greater electron density in the ring b_1 (e_1) orbital than the ring b_2 (e_1) orbital. This correlates directly with the proposition that both bonding and

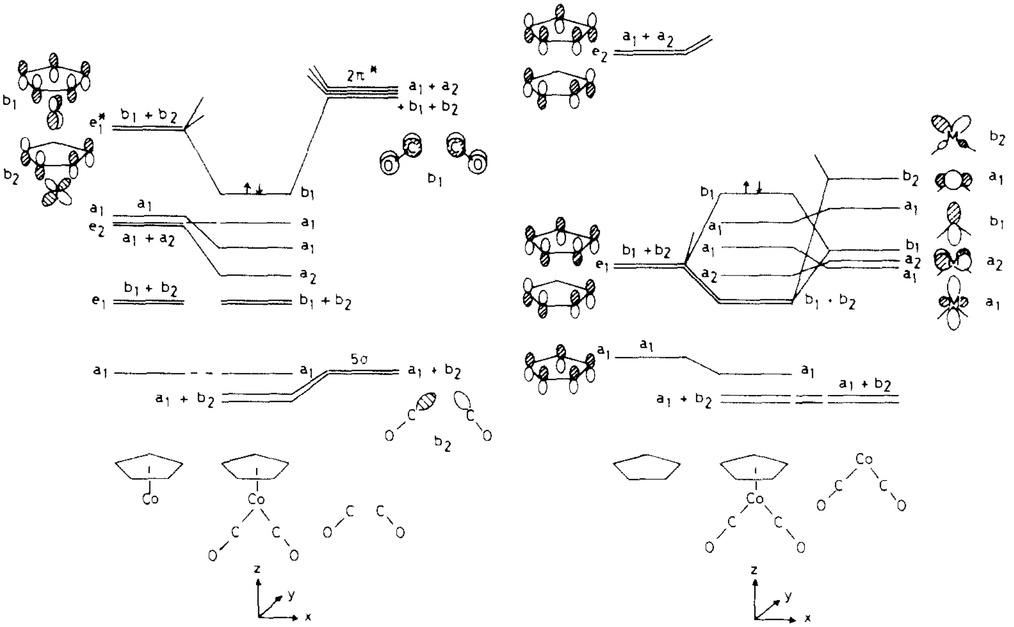

Fig. 3. Molecular orbital diagrams for $Co(\eta\text{-}C_5H_5)(CO)_2$. The left hand diagram is derived by coupling a $Co(\eta\text{-}C_5H_5)$ unit with two CO ligands; the right hand diagram is derived by joining a C_5H_5 ring with a bent $M(CO)_2$ fragment.

antibonding metal-ring b_1 orbitals are occupied whereas only the bonding b_2 orbital is occupied. (Both b_1 orbitals of course have bonding character with respect to the ring.) We observe no splitting of the ionization band (cp) associated with the ring b_1 and b_2 orbitals; however, it is reasonable that such an effect will be detectable by means of structural distortions, but insensitive to the rather blunter instrument of UV-PES.

The first ionization band has different intensity characteristics from the other *d* bands being relatively reduced in intensity in the He(II) spectra as are the cyclopentadienyl e_1 orbitals. We therefore assign it to the b_1 ionization and infer that the b_1 electrons retain some metal-ring antibonding character in the complex. The suggested assignments of the other *d*-ionization bands follow the calculation.

The ready protonation of $Co(\eta\text{-}C_5Me_5)(PMe_3)_2$ found by Werner et al. [6], is compatible with the extremely high energy of the HOMO of these phosphine complexes. Also, in the d^6 pseudo-tetrahedral products, the HOMO is non-bonding and the antibonding character of the most energetic electrons will be reduced. No stable protonation product may be obtained from $Co(\eta\text{-}C_5H_5)(CO)(PMe_3)$ [8] whereas the permethylated analogue, $Co(\eta\text{-}C_5Me_5)(CO)(PMe_3)$ will form a stable hydride cation [6].

It is interesting that Werner et al. postulate diprotonation prior to reductive elimination for $Co(\eta\text{-}C_5H_5)(PMe_3)_2$ [7]. The compound $Mo(\eta\text{-}C_6H_5Me)(PR_3)_3$, which undergoes diprotonation ($PR_3 = PMe_2Ph$, $PMePh_2$) to form a stable dication [20] has a first ionization energy of 5.3 eV ($PR_3 = PMe_3$) [21], a value very similar to those found for the pentamethylcyclopentadienyl bisphosphine complexes.

References

1 R.B.A. Pardy, D. Phil. Thesis, Oxford 1977.
2 R.B.A. Pardy and M.L.H. Green, J. Chem. Soc., Dalton Trans., (1979) 355.
3 R.B. King, A. Efraty and W.M. Douglas, J. Organomet. Chem., 56 (1973) 345.
4 R.G. Beavor, S.A. Frith and J.L. Spencer, J. Organomet. Chem., 221 (1981) C25.
5 R.B.A. Pardy, J. Organomet. Chem., 216 (1981) C29.
6 H. Werner, B. Heiser, B. Klingert and R. Dölfel, J. Organomet. Chem., 240 (1982) 179.
7 H. Werner and W. Hoffmann, Chem. Ber., 110 (1977) 3481.
8 A. Spencer and H. Werner, J. Organomet. Chem., 171 (1979) 219.
9 W.I. Bailey Jr., F.A. Cotton and J.D. Jamerson, J. Organomet. Chem., 173 (1979) 317.
10 (a) J.R. Carruthers and D.J. Watkin, CRYSTALS User Guide, Chemical Crystallography Laboratory, University of Oxford, England (1981); (b) J.R. Carruthers and D.J. Watkin, Acta. Cryst. A35, (1979) 698.
11 J.C. Green, Structure and Bonding, 43 (1981) 37.
12 E.K. Davies, CHEMGRAPH User Guide, Chemical Crystallography Laboratory, University of Oxford, England (1981).
13 L.R. Byers and L.F. Dahl, Inorg. Chem., 19 (1980) 277.
14 J.A. Kaduk and J.A. Ibers, Inorg. Chem., 16 (1977) 3283.
15 C. Cauletti, J.C. Green, M.R. Kelly, P. Powell, J. van Tilborg, J. Robbins and J. Smart, J. Electr. Spectr., 19 (1980) 327.
16 P. Hofmann, Angew. Chem. Int. Ed. Engl., 16 (1977) 536.
17 T.A. Albright and R. Hoffmann, Chem. Ber., 111 (1978) 1578; T.A. Albright, Tetrahedron, 38 (1982) 1339.
18 J.K. Burdett, J. Chem. Soc., Farad. II, 70 (1974) 1599.
19 D.M.P. Mingos, J. Chem. Soc., Dalton Trans., (1977) 602.
20 M.L.H. Green, Pure and Appl. Chem., 30 (1972) 373.
21 S.E. Jackson, D. Phil. Thesis, Oxford 1973.