Journal of Organometallic Chemistry, 397 (1990) 93–99
Elsevier Sequoia S.A., Lausanne

JOM 21076

Reactions of (η^5-$C_5H_4CO_2CH_3$)Co(CO)I_2 with polydentate phosphines

C. Moreno, M.J. Macazaga and S. Delgado

Departamento de Química (Inorgánica), Universidad Autónoma de Madrid, Cantoblanco, 28049-Madrid (Spain)

(Received April 6th, 1990)

Abstract

The reactions of (η^5-$C_5H_4CO_2CH_3$)Co(CO)I_2 with polydentate phosphines such as dppm (bis(diphenylphosphino)methane), dppe (bis(diphenylphosphino)ethane), dppa (bis(diphenylphosphino)amine), *t*-dppv (*trans*-1,2-vinylenebis(diphenylphosphine)), dpmp [bis((diphenylphosphino)methyl)phenylphosphine] and Ph_2Ppy (2-(diphenylphosphino)pyridine) yield the neutral species (η^5-$C_5H_4CO_2CH_3$)CoLI_2 (L = *t*-dppv and Ph_2Ppy), when the ligand behaves as monodentate, and monovalent cations $[(\eta^5\text{-}C_5H_4CO_2CH_3)Co(\overset{\frown}{P\ P})I]^+I^-$ ($\overset{\frown}{P\ P}$ = dppm, dppe, dppa and dpmp), when it behaves as bidentate chelate. All the compounds have been characterized by elemental analysis, conductivity measurements and IR, electronic, and ^1H and ^{31}P NMR spectroscopy.

Introduction

Dicarbonylcyclopentadienylcobalt and its analogous methyl- and pentamethylcyclopentadienyl derivatives are known to react with halogens [1,2] or pseudohalogens [3,4] to give dihalocarbonyl-π-cyclopentadienylcobalt complexes. Tertiary, ditertiary and tritertiary phosphines react rapidly with (η^5-C_5H_5)Co(CO)X_2 (X = halogen) at room temperature by replacement of the carbon monoxide or/and halogen to give neutral or ionic products, formulated as (η^5-C_5H_5)Co(phos)I_2 [1,2], [(η^5-C_5H_5)Co(diphos)I]I [5,8] or [(η^5-C_5H_5)Co(triphos)]I_2 [2,5].

There have been few studies of the reactions of dicarbonylcyclopentadienylcobalt complexes bearing electron withdrawing groups on the ring [9,10]. The complex (η^5-$C_5H_4CO_2CH_3$)Co$(CO)_2$ reacts with bidentate phosphines such as dppm, dppe, dppa, t-dppv and Ph_2Ppy to give the monosubstituted products (η^5-$C_5H_4CO_2CH_3$)Co(CO)L when L = dppm, dppa, *t*-dppv and Ph_2Ppy, while with dppe the chelate is formed. The kinetic of these substitution reactions in toluene have been studied over the temperature range 25–65 °C [11].

0022-328X/90/$03.50

We describe here the oxidative addition reactions of $(\eta^5\text{-}C_5H_4CO_2CH_3)Co(CO)_2$ with I_2 and its reactions with polydentate phosphines such as dppm, dppe, dppa, *t*-dppv, dpmp and Ph_2Ppy. The products include examples of polydentate ligands behaving as monodentate and bidentate chelate ligands. This variety of coordination patterns has been confirmed by ^{31}P NMR data.

Discussion of results

The reaction of $(\eta^5\text{-}C_5H_4CO_2CH_3)Co(CO)_2$ with iodine in ether under N_2 involves release of CO and precipitation of a solid with the stoichiometry $(\eta^5\text{-}C_5H_4CO_2CH_3)Co(CO)I_2$ (I). This compound was found to be hygroscopic and fairly soluble in solvents such as CH_2Cl_2, THF, and acetone.

Formally, the cobalt atom in I may be considered to be in the oxidation state 3 + . The resulting relatively high positive charge on the metal atom reduces the partial $d\pi\text{–}p\pi$ double bonding (backbonding) between the cobalt atom and the carbon atom of the carbonyl ligand and thus the bond order of this cobalt–carbon bond. This is reflected in the relatively high frequency of the $\nu(CO)$ band in the infrared spectrum of $(\eta^5\text{-}C_5H_4CO_2CH_3)Co(CO)I_2$ (2076.2 cm^{-1}).

On the other hand, the introduction of the electron-withdrawing carbomethoxy group into the cyclopentadienyl ring results in a shift of $\nu(CO)$ to higher frequency relative to that for the parent complex $(\eta^5\text{-}C_5H_5)Co(CO)I_2$ ($\nu(CO)$ 2045 cm^{-1}), indicating that the cobalt is less electron rich in the carbomethoxycyclopentadienyl complex.

The single carbonyl group in $(\eta^5\text{-}C_5H_4CO_2CH_3)Co(CO)I_2$ is readily replaced by other ligands at room temperature. Reaction between I and polydentate ligand such as dppm, dppe, dppa, t-dppv, dpmp and Ph_2Ppy yields the neutral species $(\eta^5\text{-}C_5H_4CO_2CH_3)CoLI_2$ (L = t-dppv and Ph_2Ppy), when the ligand functions as monodentate, and the monovalent cation $[(\eta^5\text{-}C_5H_4CO_2CH_3)Co(\overset{\frown}{P\ P})I]I$ ($\overset{\frown}{P\ P}$ = dppm, dppe, dppa and dpmp), when the ligand functions as a chelate. Their IR spectra in the 4000–200 cm^{-1} range show characteristic bands of the monosubstituted cyclopentadiene ligand with C_s symmetry [12,13]. The range of $\nu(CO)$ stretching vibrations for $(\eta^5\text{-}C_5H_4CO_2CH_3)Co(CO)I_2$ is typical of terminal ligands [14]. The bands which appear in the range 495–417 cm^{-1} correspond to ν(Co–C) and δ(Co–CO) [15]. The assignments, given in Table 1, are made on the basis of a C_s molecular symmetry.

The bands corresponding to ν(P–C) [16,17] appear in the range 690–675 cm^{-1}.

In the case of the complex $(\eta^5\text{-}C_5H_4CO_2CH_3)Co(Ph_2Ppy)I_2$ the vibrations ν(C=N) [18] (1567 and 1559 cm^{-1}) and δ(py) [19] (618 cm^{-1}) are not shifted to higher energies with respect to those for the free ligand, and thus Ph_2Ppy functions as a monodentate ligand and the coordination is through the P-atom, which is less basic than the N-atom, and this is in accord with the cobalt being a class b or soft metal.

In the complex $[(\eta^5\text{-}C_5H_4CO_2CH_3)Co(dppa)I]I$ the vibration $\nu(NH)$ (3360 cm^{-1}) is shifted, as usual, toward higher energies relative to that for the free ligand (3225 cm^{-1}). This is attributed to a change in the hybridization of the N-atom from sp^3 to sp^2 [20,21].

The ^1H and ^{31}P data for these cobalt(III) complexes are given in the experimental section. The usual down-field (high-frequency) shift of the ^{31}P resonance is observed

Table 1

IR spectral data for the complexes [a]

Complex	ν(NH)	ν(CO)(A′)	ν(CO)(CO_2CH_3)	ν(C=N)	γ(NH)	ν(PC)	δ(Co–CO)(A′)	δ(Co–CO)(A″)	ν(Co–C)(A′)
$Cp'Co(CO)I_2$		2073 vs	1734 vs				495 vs	465 vs	417 m
$Cp'Co(t\text{-dppv})I_2$			1726 vs			692 vs			
						675 sh			
$Cp'Co(Ph_2Ppy)I_2$			1726 vs	1567 m		694 vs			
				1559 m		673 sh			
$[Cp'Co(dppm)I]I$			1718 s			690 vs			
						672 sh			
$[Cp'Co(dppe)I]I$			1717 vs			691 vs			
						673 sh			
$[Cp'Co(dppa)I]I$	3360 m		1720 vs		915 vs	692 vs			
						678 sh			
$[Cp'Co(dpmp)I]I$			1726 vs			693 vs			
						676 sh			

[a] In cm^{-1}; $Cp' = \eta^5\text{-}C_5H_4CO_2CH_3$

Table 2

Electronic spectral data for the complexes [a]

Complex	$\tilde{\nu}$ max (cm^{-1})
$Cp'Co(\mathit{t}\text{-dppv})I_2$	13850, 14706, 34000, 43290
$Cp'Co(Ph_2Ppy)I_2$	16892 br, 37736, 43103
$[Cp'Co(dppm)I]I$	1456, 23900, 34602, 43103
$[Cp'Co(dppe)I]I$	15385, 22421, 35088, 43290
$[Cp'Co(dppa)I]I$	14280, 23809, 35714, 43290
$[Cp'Co(dppm)I]I$	15105, 21053, 34014, 43103

[a] $Cp' = \eta^5\text{-}C_5H_4CO_2CH_3$. CH_2Cl_2 solution

when the phosphorus is coordinated to cobalt. For each of the complexes $[(\eta^5\text{-}C_5H_4CO_2CH_3)Co(\widehat{P\ P})I]I$ ($\widehat{P\ P}$ = dppm, dppa and dppe) the spectrum consists of a singlet, shifted significantly down-field, due to the equivalence of the two P-atoms. For the complex $[(\eta^5\text{-}C_5H_4CO_2CH_3)Co(dpmp)I]I$ the ^{31}P spectrum indicates that the central P-atom is uncoordinated, showing a slight shift to higher field relative to that for the free ligand. The two equivalent terminal P-atoms have resonances significantly down-field from those for the free ligands position. For the $(\eta^5\text{-}C_5H_4CO_2CH_3)Co(t\text{-dppv})I_2$ two signals are observed, in the ranges for coordinated P and uncoordinated $^{\star}P$; in this case the signal for $^{\star}P$ is shifted slightly to lower field.

The conductivities in CH_3CN fall in the range 102–115 $ohm^{-1}\,cm^2\,mol^{-1}$, which is indicative of 1 : 1 electrolytes [22].

Electronic spectral data for the complexes in CH_2Cl_2 are shown in Table 2. These spectra display poorly resolved broad bands in the range 16892–23900 cm^{-1} due to *d–d* transitions, as a consequence of the low symmetry in the molecule, and two very intense peaks in the vicinity of 35000 and 43000 cm^{-1} due to the charge transfer transitions from the metal to the $\pi^{\star}$ orbital of ligand, or even to the $\pi^{\star}$ orbitals of the carbomethoxycyclopentadiene ligand.

Experimental

All the reactions were carried out by standard Schlenk techniques under oxygen-free N_2. The solvents, CH_2Cl_2 was refluxed over P_4O_{10} and distilled under N_2, n-hexane and diethyl ether were dried and distilled from Na in the presence of benzophenone under N_2 and CH_3CN was distilled twice from P_4O_{10} then from CaH_2. Nitrogen was bubbled through all the solvents for 1 h after they had been distilled, and they were then stored under nitrogen.

The compound $(\eta^5\text{-}C_5H_4CO_2CH_3)Co(CO)_2$ was prepared as previously described [23] and its identity confirmed by its IR and NMR spectra.

The reagents dppm [24], dppe [24], dppa [25], *t*-dppv [26], dpmp [27], and Ph_2Ppy [28] were prepared by published procedures and their identity confirmed by their IR and NMR spectra. Their melting points and elemental analyses were in good agreement with the reported values.

The cobalt was determined by titration of the Co-EDTA complex in the presence of NET as indicator. The microanalyses were performed by the Micro-analytical Laboratory of this Department. Conductivities in acetonitrile (ca. 1.0×10^{-3} *M*) were determined with a standard cell thermostated at 20 ° C, by use of a Metrohm Herisau E-518 conductometer.

The IR spectra were recorded in the range 4000–200 cm^{-1} on a Nicolet 5DX FT-IR spectrometer with Nujol or hexachlorobutadiene mulls between CsI windows or in solution in CH_2Cl_2. ^{1}H and ^{31}P NMR spectra were recorded on a Bruker WH-200-SY. The $CDCl_3$ was dried and degassed. All ^{1}H NMR chemical shifts are relative to TMS and ^{31}P chemical shifts relative to 85% aqueous H_3PO_4. The visible spectra were recorded on a Pye Unicam SP8-100 ultraviolet spectrophotometer.

Preparation of $(\eta^5\text{-}C_5H_4CO_2CH_3)Co(CO)I_2$

To a solution of $(\eta^5\text{-}C_5H_4CO_2CH_3)Co(CO)_2$ (2 g, 8.40 mmol) in Et_2O (30 ml) in a nitrogen-filled 100-ml Schlenk flask was slowly added a solution of I_2 (2.3 g, 9.06 mmol) in the same solvent. Gas evolution, accompanied by a change in color from red to violet, occurred inmediately upon mixing. The solution was stirred for several minutes during which a microcrystalline black precipitate formed. After 1 h the precipitate was filtered off, was washed with n-hexane, and dried under vacuum. The yield was 3,82 g (98%). Found: C, 20.72; H, 1.53; Co, 12.65. $C_8H_7CoO_3I_2$ calcd.: C, 20.70; H, 1.51; Co, 12.71%. ^{1}H NMR ($CDCl_3$): δ 3.94 (s, 3H, CO_2CH_3); 5.74 (s, br, 2H, H(3, 4), C_5H_4); 6.13 (s, br, 2H, H(2,5), C_5H_4).

Preparation of $[(\eta^5\text{-}C_5H_4CO_2CH_3)Co(dppm)I]I$

A solution of dppm (0,57 g, 2.16 mmol) in CH_2Cl_2 (20 ml) was added to 20 ml of a CH_2Cl_2 solution of $(\eta^5\text{-}C_5H_4CO_2CH_3)Co(CO)I_2$ (1 g, 2.16 mmol); immediate evolution of CO was accompanied by a change in color from violet-black to brown. After 2 h stirring of the solution the solvent was removed under reduced pressure. The brown residue was recrystallized from CH_2Cl_2/n-hexane (1 : 2), and the brown crystals were washed with n-hexane and dried under vacuum to yield 1.25 g (83%) of the product. Found: C, 46.68; H, 3.47; Co, 6.91. $C_{32}H_{29}CoI_2O_2P_2$ calcd.: C, 46.82; H, 3.54; Co, 7.18%. $\Lambda_M = 113\ \Omega^{-1}$ cm^2 mol^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.78 (s, 3H, CO_2CH_3); 5.07 (s, br, 2H, H(3, 4), C_5H_4); 5.96 (s, br, 2H, H(2, 5), C_5H_4); 4.11 (d, 2H, CH_2); 7.29 (m, *m*- and *p*-H, 12H, C_6H_5); 7.39 (m, *o*-H, 8H, C_6H_5). ^{31}P NMR ($CDCl_3$); δ 32.1 (s, coordinated P).

Preparation of $[(\eta^5\text{-}C_5H_4CO_2CH_3)Co(dppe)I]I$

By a similar procedure a brown solid was obtained from $(\eta^5\text{-}C_5H_4\text{-}CO_2CH_3)Co(CO)I_2$ (1 g, 2.16 mmol) and dppe (0.86 g, 2.16 mmol) in CH_2Cl_2. The yield was 1.55 g (86%). Found: C, 47.41; H, 3.38; Co, 6.86. $C_{33}H_{31}CoI_2O_2P_2$ calcd.: C, 47.50; H, 3.36; Co, 7.07%. $\Lambda_M = 105\ \Omega^{-1}$ cm^2 mol^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.85 (s, 3H, CO_2CH_3); 4.93 (s, br, 2H, H(3, 4), C_5H_4); 6.23 (s, br, 2H, H(2, 5), C_5H_4); 2.75 (m, 4H, CH_2); 7.24 (m, *m*- and *p*-H, 12H, C_6H_5); 7.46 (m, *o*-H, 8H, C_6H_5). ^{31}P NMR ($CDCl_3$): δ 81.9 (s, coordinated P).

Preparation of $[(\eta^5\text{-}C_5H_4CO_2CH_3)Co(dppa)I]I$

By a similar procedure a brown solid was obtained from $(\eta^5\text{-}C_5H_4$ $CO_2CH_3)Co(CO)I_2$ (1 g, 2.16 mmol) and dppa (0.86 g, 2.16 mmol) in CH_2Cl_2. The yield was 1.42 g (80%). Found: C, 45.37; H, 3.42; N, 1.72; Co, 6.94. $C_{31}H_{28}CoI_2NO_2P_2$ calcd.: C, 45.30; H, 3.41; N, 1.70; Co, 7.71%. $\Lambda_M = 115\ \Omega^{-1}$ cm^2 mol^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.72 (s, 3H, CO_2CH_3); 4.55 (s, br, 2H, H(3,4), C_5H_4);

5.75 (s, br, 2H, H(2, 5), C_5H_4); 3.66 (s, br, 1H, NH); 7.26 (m, 20H, C_6H_5). ^{31}P NMR ($CDCl_3$): δ 64.7 (s, coordinated P).

Preparation of [(η^5-$C_5H_4CO_2CH_3$)Co(dpmp)I]I

By a similar procedure a brown solid was obtained from (η^5-C_5H_4-CO_2CH_3)Co(CO)I_2 (1 g, 2.16 mmol) and dpmp (1.09 g, 2.16 mmol) in CH_2Cl_2. The yield was 1.67 g (82%). Found: C, 49.52; H, 3.77; Co, 6.18. $C_{39}H_{36}CoI_2O_2P_3$ calcd.: C, 49.67; H, 3.82; Co, 6.25%. $\Lambda_M = 102\ \Omega^{-1}\ cm^2\ mol^{-1}$. ^1H NMR ($CDCl_3$): δ 3.89 (s, 3H, CO_2CH_3); 4.85 (s, br, 2H, H(3, 4), C_5H_4); 6.01 (s, br, 2H, H(2, 5), C_5H_4); 3.15 (s, br, 2H, CH_2); 3.78 (s, br, 2H, CH_2); 7.36 (m, 25H, C_6H_5). ^{31}P NMR ($CDCl_3$): δ 35.7 (m, 2P, coordinated terminal P); −33.6 (s, br, 1P, unligated internal P).

Preparation of (η^5-$C_5H_4CO_2CH_3$)Co(Ph_2PPy)I_2

By a similar procedure a deep green solid was obtained from (η^5-$C_5H_4CO_2CH_3$)Co(CO)I_2 (1 g, 2.16 mmol) and Ph_2Ppy (0.57 g, 2.16 mmol) in CH_2Cl_2. The yield was 1.25 g (83%). Found: C, 40.98, H, 3.04; N, 2.12; Co, 8.45. $C_{24}H_{21}CoI_2NO_2P$ calcd.: C, 41.20; H, 3.00; N, 2.00; Co, 8.43%. ^1H NMR ($CDCl_3$): δ 3.91 (s, 3H, CO_2CH_3); 5.28 (s, br, 2H, H(3, 4), C_5H_4); 6.38 (s, br, 2H, H(2, 5), C_5H_4); 7.0 (m, 5-py, 1H, py); 7.35 (m, *m*- and *p*-H, 6H, C_6H_5); 7.57 (m, 3-, 4-py, 2H, py); 7.73 (m, *o*-H, 4H, C_6H_5); 8.87 (d, 6-py, 1H, py). ^{31}P NMR ($CDCl_3$): δ 35.8 (s, coordinated P).

Preparation of (η^5-$C_5H_4CO_2CH_3$)Co(t-dppv)I_2

By a similar procedure a green solid was obtained from (η^5-C_5H_4-CO_2CH_3)Co(CO)I_2 (1 g, 2.16 mmol) and *t*-dppv (0.86 g, 2.16 mmol) in CH_2Cl_2. The yield was 1.56 (87%). Found: C, 47.11; H, 3.50; Co, 6.99. $C_{33}H_{29}CoI_2O_2P_2$ calcd.: C, 47.59; H, 3.48; Co, 7.08%. ^1H NMR ($CDCl_3$): 3.94 (s, 3H, CO_2CH_3); 4.41 (s, br, 2H, H(3, 4), C_5H_4); 5.88 (s, br, 2H, H(2, 5), C_5H_4); 7.24 (t, 2H, CH=CH); 7.45 (m, *m*- and *p*-H, 12H, C_6H_5), 7.82 (m, *o*-H, 8H, C_6H_5). ^{31}P NMR ($CDCl_3$): 39.5 (s, coordinated P); −2.8 (s, unligated P).

Acknowledgements

We thank Dr. Jesús H. Rodriguez Ramos for the ^{31}P NMR spectra.

References

1 R.F. Heck, Inorg. Chem., 4 (1965) 855; idem, ibid, 7 (1968) 1513.
2 R.B. King, Inorg. Chem., 5 (1966) 82.
3 S. Delgado, M.J. Macazaga and J.R. Masaguer, J. Organomet. Chem., 268 (1984) 79; idem, ibid, 259 (1983) 233.
4 S. Delgado, M.J. Macazaga, C. Moreno and J.R. Masaguer, J. Organomet. Chem., 289 (1985) 397.
5 R.B. King, L.W. Houk and K.H. Pannell, Inorg. Chem., 8 (1969) 1042.
6 S.J. Landon and T.B. Brill, Inorg. Chem., 29 (1984) 1266.
7 Q.-B. Bao, S.J. Landon, A.L. Rheingold, T.M. Haller and T.B. Brill, Inorg. Chem., 24 (1985) 900.
8 E.E. Isaacs, W.A.G. Graham, J. Organomet. Chem., 120 (1976) 407.
9 W.P. Hart, D. Shihua and M.D. Rausch, J. Organomet. Chem., 282 (1985) 111.
10 W.P. Hart and M.D. Rausch, J. Organomet. Chem., 355 (1988) 455.
11 C. Moreno, M.J. Macazaga and S. Delgado, submitted.

12 D.M. Adams and A. Squire, J. Organomet. Chem., 63 (1973) 381.
13 D.J. Parker, Spectrochim. Acta A, 31 (1975) 1789.
14 D.M. Adams, Metal–Ligand and Related Vibrations, St. Martin's Press, New York, 1967, Ch. 3.
15 L.M. Haines and M.H.B. Stiddard, Adv. Inorg. Chem. and Radiochem., 12 (1969) 53.
16 H.G. Horn and K. Sommer, Spectrochimica Acta A, 27 (1971) 1049.
17 M. Bacci, Spectrochimica Acta A, 28 (1972) 2286.
18 J.K. Wilmshurst and H.J. Bernstein, Can. J. Chem., 35 (1965) 31.
19 R.J.H. Clark and C.S. Williams, Inorg. Chem., 4 (1965) 350.
20 J. Ellermann, N. Geneeb, G. Zaubek and G. Thiele, Z. Naturforsch. B, 32 (1977) 1271.
21 R. Usón, J. Fornies, R. Navarro and J.I. Cebollada, J. Organomet. Chem., 304 (1986) 381.
22 W. Geary, J. Coord. Chem. Rev., 7 (1971) 81.
23 W.P. Hart, D. Shihua and M.D. Rausch, J. Organomet. Chem., 282 (1985) 111.
24 W. Hewertson and H.R. Watson, J. Chem. Soc., 4 (1962) 1490.
25 H. Nöth and L. Meinel, Z. Anorg. Allg. Chem., 349 (1967) 225.
26 A.M. Aguiar and D. Daigle, J. Am. Chem. Soc., 86 (1964) 2299.
27 R. Appel, K. Geisler and H.F. Scholer, Chem. Ber., 112 (1979) 648.
28 A. Maisonnet, J.P. Farr, M.M. Olmstead, C.T. Hunt and A.L. Balch, Inorg. Chem., 21 (1982) 3961.