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CARBONYLVANADIUM COMPLEXES OF THE TRIPOD LIGANDS $MeC(CH_2PPh_2)_3$ AND $P(CH_2CH_2PPh_2)_3$

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Summary

UV irradiation of $[Et_4N][V(CO)_6]$ in the presence of the tripod ligands (L) $MeC(CH_2PPh_2)_3$ (cp_3) and $P(CH_2CH_2PPh_2)_3$ (pp_3) yields $[Et_4N][V(CO)_5L]$, *cis*-$[Et_4N][V(CO)_4L]$ and *mer*-$[Et_4N][V(CO)_3L]$ (where the *meridional* configuration for L = cp_3 is uncertain). Except for $[Et_4N][V(CO)_5cp_3]$, all these species were isolated. The complexes are characterized by their IR, ^{31}P and ^{51}V NMR spectra.

Introduction

There is only restricted information on the coordinative properties of the potentially tri- and tetra-tertiary tripod ligands $MeC(CH_2PPh_2)_3$ (cp_3) and $P(CH_2CH_2PPh_2)_3$ (pp_3) see e.g. [1] and [2]). In octahedral transition metal carbonyl complexes, cp_3 tends replace three CO groups in *facial* positions, as shown by the IR pattern in the CO stretching region of the complexes $M(CO)_3cp_3$ (M = Cr, Mo, W) [3] and $V(CO)_3cp_3$ [4]. pp_3 reacts with group VIb hexacarbonyls and $XMn(CO)_5$ (X = Me, Br) to $M(CO)_3pp_3$ and $XMn(CO)_2pp_3$ [5]. In $Cr(CO)_3pp_3$, the ligand is coordinated via the alkyl-phosphorus and two terminal PPh_2 groups [6]. pp_3 may also act as a tetradentate ligand. This is confirmed by the existence of $M(CO)_2pp_3$ (M = Mo, W) [5] and *cis*$[HV(CO)_2pp_3]$ [7].

Extending our investigations on carbonylvanadium complexes of the linear tri- and tetratertiary phosphines $PhP(CH_2CH_2PPh_2)_2$ (p_3) and $(Ph_2PCH_2CH_2PPhCH_2)_2$ (p_4), which form *cis*-di- and *mer*-tri-substituted carbonylphosphinevanadates(—I) [8,9], we describe here the preparation and properties of anionic complexes of the tripod ligands. Carbonylvanadates(—I) containing mono- or oligodentate phosphines are reactive and have been satisfactorily employed in the preparation of η^3-allyl [10] and hydrido complexes [7,11].

TABLE 1

ANALYTICAL DATA AND SELECTED PROPERTIES [a]

		Empirical formula (molecular mass)	Analysis (found (calcd.) (%))				
			C	H	N	P	V
$[Et_4N][V(CO)_4cp_3]$ (I)	crystalline, orange powder	$C_{53}H_{59}NO_4P_3V$ (917.93)	68.9 (69.35)	6.8 (6.48)	1.5 (1.53)	9.8 (10.12)	5.2 (5.55)
$[Et_4N][V(CO)_3cp_3]$ (II)	black, brittle plates	$C_{52}H_{59}NO_3P_3V$ (889.92)	69.8 (70.18)	6.9 (6.68)	1.8 (1.57)	9.9 (10.44)	5.8 (5.72)
$[Et_4N][V(CO)_5pp_3]$ (III)	yellow to yellow-orange needles	$C_{55}H_{62}NO_5P_4V$ (991.95)	66.6 (66.60)	6.1 (6.30)	1.5 (1.41)	*b*	*b*
$[Et_4N][V(CO)_4pp_3]$ (IV)	orange to orange-red powder	$C_{54}H_{62}NO_4P_4V$ (963.94)	67.0 (67.29)	6.6 (6.48)	1.6 (1.45)	12.5 (12.85)	5.1 (5.28)
$[Et_4N][V(CO)_3pp_3]$ (V)	wine-red powder	$C_{53}H_{62}NO_3P_4V$ (935.93)	67.6 (68.02)	6.9 (6.68)	1.6 (1.50)	13.1 (13.24)	5.8 (5.44)

[a] cp_3 = $MeC(CH_2PPh_2)_3$; pp_3 = $P(CH_2CH_2PPh_2)_3$. [b] CHN values only due to small yields.

Experimental

General method and materials

All operations were carried out under nitrogen and in anhydrous, oxygen-free solvents. For UV irradiation, an irradiation apparatus of 100 ml capacity (DEMA 13/21, Mangels, Bonn), consisting of a cylindrical vessel fitted with a cooling mantle and a quartz immersion well was used. UV source was a high-pressure mercury lamp (Philips HPK 125, Mangels). During the irradiation, the solution was agitated by passing a weak N_2-stream through a filter plate at the bottom of the reaction vessel. N_2, and CO generated in the course of the reaction, were released via a 20 mm mercury valve. The phosphine ligands were obtained from commercial sources (Strem); $[Et_4N][V(CO)_6]$ was prepared as described previously [8].

Spectroscopic measurements

IR: ca. 0.02 *M* THF or THF/CH_3CN solutions in 0.1 KBr cuvettes; Perkin—Elmer spectrometer 337; absolute error ±1 to ±3 cm^{-1}. ^{51}V NMR: ca. 0.1 *M* THF or THF/CH_3CN solutions in rotating 7.5 mm diameter vials fitted into 10 mm tubes containing $CDCl_3$ as external lock; 23.66 MHz, Bruker WH 90 PFT spectrometer; standard $VOCl_3/CDCl_3$ 2/1; absolute error ±3 ppm at constant temperature (298 K). $^{31}P\{^1H\}$: ca. 0.1 *M* THF or THF/CH_3CN solution in rotating 7.5 mm diameter vials; 36.44 MHz, Bruker WH 90 PFT spectrometer; external standard H_3PO_4 80%, external lock $CDCl_3$; absolute error ±1 to ±3 ppm (broad signals) and ±0.1 ppm (narrow signals) at constant temperature (202 ± 2 K).

Analytical data and some of the properties are listed in Table 1.

cis-Tetraethylammonium tetracarbonyl-1,1,1-tris(diphenylphosphinomethyl)-ethanevanadate(—I), cis-$[Et_4N][V(CO)_4CH_3C(CH_2PPh_2)_3]$ (I) and tetraethylammonium tricarbonyl-1,1,1-tris(diphenylphosphinomethyl)ethanevanadate(—I), $[Et_4N][V(CO)_3CH_3C(CH_2PPh_2)_3]$ (II)

0.91 g $[Et_4N][V(CO)_6]$ (2.6 mmol) and 1.62 g phosphine (2.6 mmol) dissolved in 100 ml THF were irradiated for 5.5 hours. Precipitation of orange-red I commenced after 4 hours and was complete after a further 1.5 hours of irradiation. At this time, most of the I remaining in solution was converted to II. The residue and solution were separated immediately by decantation and filtration. The residue was washed with 5 ml THF, dissolved in 30 ml CH_3CN, concentrated to 5 ml (in vacuo at room temperature), diluted with THF to 30 ml and allowed to stand for 5 days at 273 K. The orange, crystalline I thus obtained was filtered off and dried under high vacuum (3 hours).

The filtrate containing I and II was allowed to stand at 273 K for several days. Black thin plates of II separated, and after decantation of the supernatent solution, they were dried under vacuum. A mixture of I and II was obtained from the mother liquor on further standing.

Tetraethylammonium pentacarbonyltris(2,2-diphenylphosphinoethyl)phosphinevanadate(—I), $[Et_4N][V(CO)_5P(CH_2CH_2PPh_2)_3]$ (III), cis-tetraethylammonium tetracarbonyltris(2,2-diphenylphosphinoethyl)phosphinevanadate(—I),

cis-[Et$_4$N][V(CO)$_4$P(CH$_2$CH$_2$PPh$_2$)$_3$] (IV), and mer-tetraethylammonium tricarbonyltris(2,2-diphenylphosphinoethyl)phosphinevanadate(—I), mer-[Et$_4$N]-[V(CO)$_3$P(CH$_2$CH$_2$PPh$_2$)$_3$] (V)

A solution of 0.60 g [Et$_4$N][V(CO)$_6$] (1.72 mmol) and 1.21 g phosphine (1.80 mmol) in 100 ml THF was irradiated for 75 min. The solution was halved, and one of the portions was concentrated to 5 ml, treated with 5 ml of toluene and 10 ml of heptane. A dark red, sticky product separated. After decantation of the supernatent yellow solution, the residue was dissolved in 5 ml THF and IV was repricipitated with toluene/heptane. Half an hour of stirring yielded an orange coloured powdery product, which was filtered off, washed three times with 10 ml portions of toluene/heptane 1/2, and dried under high vacuum.

The second portion was diluted with THF to ca. 100 ml and irradiated for 7 hours, concentrated to 5 ml and allowed to stand at 245 K for 3 days, whereupon V partly crystallized. To complete the precipitation, three ml of heptane were added dropwise with vigorous stirring. The precipitate was filtered off after 10 min of stirring, washed twice with 5 ml portions of heptane, and dried to yield the wine-red V.

Small amounts of III can be obtained in the following manner: A THF solution containing about 1 mmol of the reactants is irradiated for 10 min. After that time the solution contains III, IV and unchanged hexacarbonylvanadate(—I). The solution is concentrated to 5 ml and passed through a silica gel column (12 × 3 cm, for details see [11]), using 40 ml THF as eluant, followed by 30 ml THF/CH$_3$CN 3/2 and 40 ml CH$_3$CN. The solution drawn off the column (the total time for elution should not exceed 45 min) contains III and a mixture of HV(CO)$_3$pp$_3$ and HV(CO)$_4$pp$_3$ [7]. The solution is immediately evaporated to about one third of its original volume, treated cautiously with heptane until slightly turbid and allowed to stand at 245 K for two weeks. During this time, small yellow needles of III separate out, and, after decantation of the liquid phase they are dried under high vacuum. Further III is obtained from the decantate by addition of 20 ml heptane. This portion is, however, slightly contaminated by the hydrido complexes.

Results and discussion

Preparation and properties

The di- and tri-substituted complexes are prepared by UV irradiation of THF solution containing the starting products ([Et$_4$N][V(CO)$_6$] and phosphine) in equimolar amounts. Substitution of the first CO group is completed after about 15 min. Disubstitution starts simultaneously. Average irradiation times for optimal yields of disubstitution product is ca 1 hour (IV) and four hours (I), respectively. For complete removal of a third CO group, ca. 7 hours are needed. The trisubstituted species are thermolabile and extremely sensitive to oxygen in solution. The solids are pyrophoric. With pp$_3$, no tetra-substituted product is obtained, which is in accord with analogous observations for the reaction between [V(CO)$_6$]$^-$ and p$_4$ [8]. Further irradiation results in gradual decomposition of the product. The coordinative behaviour of pp$_3$ towards hexacarbonylvanadate(—I) thus differs from that observed for the carbonylmolybdenum(0) [5] and carbonylhydridovanadium(0) [7] compounds, where 4 CO groups can be substituted. The lower formal oxidation state of vanadium in the anionic compound does not allow for the substitution of a fourth CO due to less sufficient π-electron delocalization ability of the π-accepting orbitals located on the phosphine.

The monosubstitution products, which are identified by their IR pattern after short irradiation times, are not easily isolated. In the case of pp$_3$, small amounts of pure $[Et_4N][V(CO)_5pp_3]$ (III) can be obtained by removal of the disubstituted species IV and unsubstituted $[Et_4N][V(CO)_6]$ through chromatography on silica gel. While IV is easily converted to $HV(CO)_4pp_3$ and further to $HV(CO)_3pp_3$ [7], the conversion of III into the hydrido complex occurs at sufficiently slow rates. $[Et_4N][V(CO)_6]$ remains on the silica gel carrier, and from the eluant (containing III and hydrido complexes), III is isolated by fractional crystallization.

Spectra

Spectroscopic data are compiled in Table 2. For comparison, data on the di- and trisubstituted complexes of the linear phosphines p$_3$ (from [9]) and p$_4$ (from [8]) are added.

The ^{31}P NMR spectrum of III shows, in addition to the broad signals associated with coordinated phosphorus, a strong doublet at —14.6 ppm [$^3J(^{31}P—^{31}P)$

TABLE 2

CO-STRETCHING FREQUENCIES, ^{31}P AND ^{51}V NMR DATA

Complex	ν(CO) (cm^{-1}) [a]	$\delta(^{51}V)$ [b] (ppm)	$\delta(^{31}P)$ [c] (ppm) coordinated	$\delta(^{31}P)$ [c] (ppm) uncoordinated [d]
$[V(CO)_5cp_3]^-$ [e]	1965 1820 1857	—1820	+53	—28.7
cis-$[V(CO)_4cp_3]^-$ (I)	1894 (1785) 1766 (1750)	—1733	+27	—29.2
$[V(CO)_3cp_3]^-$ (II)	1910 1798 1705	—1729	+40	
$[V(CO)_5pp_3]^-$ (III)	1962 1814 1852	—1849, —1885 [f]	+99, +97, +87, +83	—14.6 (d, 29.5), —17.9 [g]
cis-$[V(CO)_4pp_3]^-$ (IV)	1893 1788 (1770) (1740)	—1820	ca. +65 [h]	—14.5 (d, 29.5)
mer-$[V(CO)_3pp_3]^-$ (V)	1913 1807 1713	—1724	ca. +77 [h]	—14.6 (d, 29.7)
cis-$[V(CO)_4p_3]^-$ (VI) [i]	1903 1800 (1770) (1740)	—1830 [j]	+68, +83	—16.4 (d, 31)
cis-$[V(CO)_4p_4]^-$ (VII) [k]	1896 1792 1770 1733	—1790	[l],[m]	—13.5, —17.3 [l]
mer-$[V(CO)_3p_3]^-$ (VIII) [i]	1910 1805 1714	—1720	+62, +87	
mer-$[V(CO)_3p_4]^-$ (IX) [k]	1898 1810 1715	—1810	[l],[m]	—12.0 (d, 29), –15.9 (t, 25) [l]

[a] In ca. 0.01—0.02 *M* CH_3CN (I, II), CH_3CN/THF (IV) or THF (other). Relative intensities: Monosubstitution (w, s, s-vs), disubstitution (m, s, vs, s), trisubstitution (vw-w, s, s); bands in brackets are shoulders. [b] Ca. 0.1 *M* THF or THF/CH_3CN upfield $VOCl_3$, 298 K. [c] Ca. 0.1 THF or THF/CH_3CN relative to H_3PO_4 80%, 202 K. [d] Free ligand (at room temperature): $MeC(CH_2PPh_2)_3$(cp$_3$) — 27.5 (t, 2.4; see [18]); $PhP(CH_2CH_2PPh_2)_2$(p$_3$) —16.6 (PPh, t) and —12.8 (PPh$_2$, d), J(PP) = 29.1 [17]; $(Ph_2PCH_2CH_2PPhCH_2)_2$(p$_4$) —16.7 (PPh, t) and —12.8 (PPh$_2$, d), J(PP) = 28.9 and 24.0 [17]; $P(CH_2CH_2PPh_2)_3$(pp$_3$) (in CH_2Cl_2) —12.85 (PPh$_2$, d) and —17.15 (P, q), J(PP) = 25.3 ± 0.6. [e] Not isolated. [f] —1849: V—P; —1885: V—PPh$_2$. [g] Uncoordinated central phosphorus (weak, unresolved signal). [h] Unresolved eight-line system (see text). [i] From [9]. [j] Triplet, J(VP) = 223 Hz. [k] From [8]. [l] At room temperature. [m] Not observed.

29.5 Hz] and a weak, unresolved signal centered at —17.9 ppm. The former is to be assigned the PPh_2 groups, the latter to the central $P(CH_2CH_2—)_3$ portion of the ligand. Thus, pp_3 is chiefly bonded via the PPh_2 group. Accordingly, the main signal in the ^{51}V NMR spectrum is at $\delta(^{51}V) = 1885$ ppm, while a shoulder at —1849 ppm indicates that there is also a species present, where the ligand is coordinated via the alkylphosphine. It has been shown for PPh_3 and PEt_3 complexes of $[V(CO)_6]^-$ and η^5-$C_5H_5V(CO)_4$ that the ^{51}V signals of alkylphosphine-vanadium complexes appear at lower fields [12].

The ^{31}P NMR signals of the uncoordinated P-atoms in the complexes IV and V clearly indicated that pp_3 is bonded via PPh_2 and P. The five-membered chelate ring is thus preferred, as observed for $Cr(CO)_4pp_3$ and $Cr(CO)_3pp_3$ [6]. Since an eight-membered ring system is no more strained than a five-ring, the favoured five-ring structure may be account for either in terms an easier approach of the central P on a time-averaged scale, or of the stronger ligating power of a trialkylphosphine relative to a diphenylalkylphosphine as established by ^{51}V NMR [12]. The five-ring is also the basic structural unit in complexes with the linear p_3 and p_4, but there is also evidence for chelate eight-rings with these ligands ($[V(CO)_4p_4]^-$ [8] and η^5-$C_5H_5V(CO)_2p_3$ [9]).

Another interesting NMR feature of IV and V is the broad, plateau-like ^{31}P NMR signal for the coordinated P-atoms. This pattern is typical of a dipolar nucleus (^{31}P) coupling with a quadrupolar nucleus (^{51}V, I 7/2) and was also observed in the ^1H NMR spectrum of $[\eta^5$-$C_5H_5V(H)(CO)_3]^-$ [7]. The expected line system (eight equidistant signals of equal intensity) is, however, unresolved because of quadrupolar line broadening. From the overall width of 1200 Hz, one can estimate the $^{31}P—^{51}V$ nuclear spin—spin coupling constant to approximately 150 Hz, which is about the same magnitude as that of the directly measured $^{51}V—^{31}P$ coupling in the ^{51}V NMR spectra of complexes of mono- and ditertiary phosphines [8,12,13]. In I to III, spin—spin coupling is widely depressed and the ^{31}P resonances are reduced to broad Lorentzian signals (half widths several hundred Hz). The same is true for VI and VIII.

One would expect a facial arrangement of the tripod ligand cp_3 in trebly substituted pseudo-octahedral complexes, and this geometry was confirmed in carbonylchromium(0) and carbonylvanadium(0) complexes [3,4] and also in $HV(CO)_3cp_3$ [7]. The local symmetry of a complex *fac*-$[V(CO)_3cp_3]^-$ is C_{3v}. The IR spectrum should exhibit two $\nu(CO)$ absorptions. However, the same pattern (three $\nu(CO)$ frequencies) is observed as in V, VIII and IX, all of which show the three modes for *meridional* configuration (local C_{2v} symmetry). Since II cannot achieve this configuration without considerable strain in the molecule, it seems more likely that the original facial configuration is distorted to an extent where the degeneracy of the E-mode in C_{3v} is completely raised.

Distortions are supposed to be reflected in low-field ^{51}V shielding and (as has been pointed out by several authors for ditertiary phosphine complexes) in comparatively high ^{31}P shielding for the coordinated phosphorus, i.e. small phosphorus coordination shifts $\Delta(\delta_P)$ [14—16]. We have observed maximum $\Delta(\delta_P)$ values parallelled by maximum ^{51}V shielding in chelate five-rings of carbonylvanadium compounds of bis(phosphines) $Ph_2P(CH_2)_nPPh_2$ (n = 1—4) [8], and a down-field ^{51}V shift and decreased $\Delta(\delta_P)$ for chelate six-rings. The same trend is observed in I (6-ring) as compared to the 5-ring systems IV, VI and VII.

However, there is no further down-field shift for II relative to I, or V and VIII. Hence, there is no indication from the NMR spectra as to substantial distortions of the inter-bond angles in II. This discrepancy cannot at present be accounted for, and the question of whether $[V(CO)_3cp_3]^-$ is to be assigned a *meridional* or *facial* configuration remains open.

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References

1 B. Chiswell, in C.A. McAuliffe (Ed.), Transition Metal Complexes of Phosphorus, Arsenic and Antimony, MacMillan, London, 1973, p. 274.
2 R. Mason and D.W. Meek, Angew. Chem., 90 (1978) 195.
3 J. Chatt and H.R. Watson, J. Chem. Soc., (1961) 4980.
4 H. Behrens and K. Lutz, Z. Anorg. Allg. Chem., 356 (1967) 225.
5 R.B. King, R.N. Kapoor, M.S. Saran and P.N. Kapoor, Inorg. Chem., 10 (1971) 1841.
6 R.B. King and J.C. Cloyd, Jr., Inorg. Chem., 14 (1975) 1550.
7 U. Puttfarcken and D. Rehder, J. Organometal. Chem., 185 (1980) 219 .
8 D. Rehder, L. Dahlenburg and I. Müller, J. Organometal. Chem., 122 (1976) 53.
9 I. Müller and D. Rehder, J. Organometal. Chem., 139 (1977) 293.
10 U. Franke and E. Weiss, J. Organometal. Chem., 121 (1976) 355; ibidem, 153 (1978) 39.
11 U. Puttfarcken and D. Rehder, J. Organometal. Chem., 157 (1978) 321.
12 R. Talay and D. Rehder, Chem. Ber., 111 (1978) 1978.
13 D. Rehder, W.L. Dorn and J. Schmidt, Trans. Met. Chem., 1 (1976) 233.
14 S.O. Grim, W.L. Briggs, R.C. Barth, C.L. Tolman and J.P. Jesson, Inorg. Chem., 13 (1974) 1095.
15 D.E. Edwards and J. Marshalsea, J. Organometal. Chem., 96 (1975) C50.
16 T.G. Appleton, M.A. Bennett and I.B. Tomkins, J. Chem. Soc. Dalton Trans., (1976) 439.
17 D.L. DuBois, W.H. Myers and D.W. Meek, J. Chem. Soc. Dalton Trans., (1975) 1011.
18 R.M. Kirchner, R.G. Little, K.D. Tau and D.W. Meek, J. Organometal. Chem., 149 (1978) C15.