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Structure of (μ_3-CCl)Co$_3$(CO)$_7$(μ-dppm); a Chloroalkylidyne Capped Tricobalt Cluster with a Bidentate Bis(diphenylphosphino)methane Ligand Bridging One Edge of the Tricobalt Triangle

By D. Neil Duffy,* Maram M. Kassis and A. David Rae

School of Chemistry, University of New South Wales, PO Box 1, Kensington NSW, 2033 Australia

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Abstract. Heptacarbonyl-μ_3-chloromethylidyne-μ_2-[methanediylbis(diphenylphosphino)-*P*,*P*′]tricobalt-(3*Co*–*Co*) isopentane solvate, [Co$_3$(CCl)(C$_{25}$H$_{25}$P$_2$)-(CO)$_7$].C$_5$H$_{12}$, M_r = 876·83, triclinic, $P\bar{1}$, a = 12·050 (6), b = 12·758 (6), c = 13·076 (6) Å, α = 95·88 (3), β = 101·12 (3), γ = 100·55 (3)°, V = 1919 (1) Å^3, Z = 2, D_x = 1·52, D_m(flotation) = 1·49 g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, μ(Mo $K\alpha$) = 14·71 cm^{-1}, F(000) = 892, T = 295 K, R = 0·054 for 4774 independent reflections with $I > 3\sigma(I)$. (μ_3-CCl)Co$_3$(CO)$_7$(μ-dppm) is the product of the reaction of bis(diphenylphosphino)methane (dppm) and chloroalkylidynenonacarbonyltricobalt (μ_3-CCl)Co$_3$-(CO)$_9$. A disordered solvent molecule (isopentane) was included in the calculations using back Fourier transform methods. The structure contains a triangle of Co atoms capped by the chloroalkylidyne unit, and with one of the edges of the Co triangle bridged by the dppm unit. The Co—Co distances range from 2·483 (1) to 2·492 (1) Å. The other dimensions of major interest are Co—P 2·200 (3) Å and Co—C(Cl) which range from 1·901 (5) to 1·858 (3) Å.

Introduction. (μ_3-CCl)Co$_3$(CO)$_7$(μ-dppm) (1) is one of a number of alkylidene tricobalt clusters containing a bidentate phosphine ligand synthesized recently (Downard, Robinson & Simpson, 1986; Balavione, Collin, Bonnet & Lavigne, 1985; Aime, Botta, Gobetto, Osella & Molone, 1987; Bruce, Kehoe, Matisons, Nicholson, Rieger & Williams, 1982). Few have been fully characterized by X-ray crystallography. This paper reports the crystal and molecular structure of (1) synthesized by the benzophenone ketyl radical anion catalyzed reaction of (μ_3CCl)Co$_3$(CO)$_9$ with dppm. The structure can be compared with the methyl analogue (2), the structure of which has been determined twice (Balavione *et al.*, 1985; Downard *et al.*, 1986). Values given here for (2) are mean values unless otherwise stated.

Experimental. (μ_3-CCl)Co$_3$(CO)$_7$(μ-dppm) crystallizes as black crystals (Bruce *et al.*, 1982). An irregular crystal of maximum dimensions 0·28 × 0·29 × 0·09 mm was mounted on a quartz fiber and the lattice parameters (T = 295 K, 24 reflections θ range 18–23°) were determined and refined with the least-squares routine on an Enraf–Nonius CAD-4 four-circle diffractometer equipped with a graphite monochromator.

A total of 6741 unique reflections (6917 measured reflections) were collected in the range $1·50 < \theta < 25·0°$ using an ω–2θ scan mode. $-14 < h < 13$, $-15 < k < 15$, $0 < l < 15$. The intensity of one standard reflection was measured after every 2000 s of X-ray exposure. Approximately 17% decomposition occurred during data collection. Lorentz, polarization and absorption corrections (Gaussian integration method, maximum and minimum transmission factors were 0·874 and 0·679 respectively) were applied to all reflections using locally written programs. 4774 independent reflections with $I > 3\sigma(I)$ were used in the structure refinement calculations (on F) using *RAELS*88 (Rae, 1984). Scattering factors for neutral atoms were obtained from Ibers & Hamilton (1974).

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* Author to whom correspondence should be addressed.

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The atomic coordinates of the three Co atoms were determined from a Patterson map. The associated and subsequent difference Fourier maps revealed all non-H atoms (except the disordered solvent molecule) in chemically reasonable positions. With all non-H atoms anisotropic and H atoms included in calculated positions, the refinement based on 288 parameters converged at $R = 0{\cdot}073$ and $wR = 0{\cdot}123$ respectively $\{w = 1/\sigma^2(F_o)$ where $\sigma^2(F_o)$ was derived from $[\sigma^2(I_o) + 0{\cdot}04I_o^2]^{1/2}\}$. $\Delta/\sigma_{\max} < 1$ and $\Delta\rho_{\max} \simeq 1{\cdot}0\ \text{e}\ \text{Å}^{-3}$ and is associated with the metal triangle. The presence of a solvent molecule (isopentane) was indicated by a Fourier map which showed electron density within the cavity resulting from the packing of the dppm ligands. This is also indicated by the elemental analysis and an NMR spectrum of a sample of (1). Attempts to model the solvent electron density as an ordered molecule gave a chemically unreasonable fragment. The solvent electron density in the structure was back Fourier transformed using the method developed by Rae & Baker (1984). Constrained refinement was undertaken using the program *RAELS*88 (Rae, 1984). Two of the four phenyl rings were disordered. A refineable local planar geometry of *mm*2 symmetry was assumed to be common to all the phenyl rings. The positions and orientations of the phenyl rings were also refined. Thermal motion of the phenyl rings was described using *TL* models with the centres of libration centred on the P atom to which the rings are attached. The *TL* parameters were considered common to both orientations as the disordered ring occupancies were fixed at 0·5. Restraints [(slack constraints) (Rae, 1984)] were also applied to the disordered phenyl rings to ensure sensible geometry. The disordered rings were restrained so that the connected P atom lies as close as possible to the twofold axes of the phenyl rings and at equal distances from the connecting atoms in the rings.

Refinement using this technique led to final agreement indices of $R = 0{\cdot}054$ and $wR = 0{\cdot}067$.

Fig. 1 shows the molecular structure of (1) and the numbering scheme employed (*ORTEP*II, Johnson, 1976). Atomic coordinates and the mean thermal parameters $(U_{11} + U_{22} + U_{33})/3$ are given in Table 1.* Table 2 lists selected bond lengths and bond angles.

Discussion. The structure consists of a triangle of Co metals capped by a chloroalkylidene unit with one of the edges of the metal triangle bridged by a bidentate dppm unit. The Co—Co distances in the triangle range from 2·483 (1) to 2·492 (1) Å. This variation is significant, with the longer of the three Co—Co bonds being the one bridged by the phosphine ligand as also observed in the methyl analogue $[(\mu_3\text{-CCH}_3)\text{Co}_3(\text{CO})_7(\mu\text{-dppm})]$ (2), where the variation is rather more pronounced, 2·470 (4) Å for non-bridged and 2·488 (4) Å for bridged.

The Co—C_{apical} [Co—C(123)] distances vary quite markedly, as noted previously for (2). The unbridged Co—apical atom distance of 1·901 (5) Å [Co(3)—C(123)] is shorter than for the equivalent bond in (2) [1·954 (5) Å]. The other two Co—C_{apical} distances are essentially equal at 1·860 (5) and 1·857 (5) Å. These are similar to those found previously. However, the variation in the values is less than that observed for (2), *i.e.* 1·860 (6), 1·887 (5) Å (Downward *et al.*, 1986) and 1·887 (5), 1·82 (1) Å (Balavione *et al.*, 1985) respectively. It is in these Co—C_{apical} distances that the two determinations of (2) vary most. This asymmetry in the bonding to the apical C atom has only been observed in the methyl analogue and this structure, *i.e.* the dppm substituted clusters. Other $R\text{CCo}_3(\text{CO})_{9-n}L_n$ [$L = \text{PPh}_3$, P(OMe)_3] structures have not shown this marked deviation from a symmetrical capping configuration (Downward *et al.*, 1986; Bruce, Penfold, Robinson & Taylor, 1970; Dawson, Robinson & Simpson, 1979; Matheson & Penfold, 1977; Penfold & Robinson, 1973). The displacement of the carbyne C atom toward the phosphine bridge is accompanied by a displacement of the Cl atom towards the unbridged Co atom [the angles are Co(1)—C(123)—Cl 132·0 (3), Co(2)—C(123)—Cl 131·2 (3) and Co(3)—C(123)—Cl

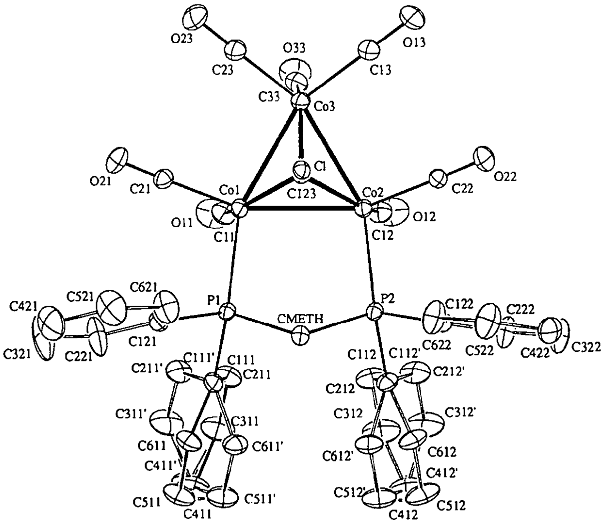

Fig. 1. The molecular structure of $(\mu_3\text{-CCl})\text{Co}_3(\text{CO})_7(\mu\text{-dppm})$ and the numbering scheme used (*ORTEP*II).

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond angles and selected torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53823 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates, thermal parameters* $(U_{11} + U_{22} + U_{33})/3$ (Å^2) *and e.s.d.'s for the non*-H *atoms of* (μ_3-CCl)Co$_3$(CO)$_7$(μ-dppm)

	x	y	z	$(U_{11} + U_{22} + U_{33})/3$
Co(1)	0·34908 (6)	0·13349 (5)	0·38270 (5)	0·040 (0)
Co(2)	0·17772 (6)	0·21661 (5)	0·38532 (5)	0·039 (0)
Co(3)	0·26013 (7)	0·13348 (6)	0·53888 (5)	0·048 (0)
Cl	0·4171 (1)	0·3708 (1)	0·5340 (1)	0·060 (0)
P(1)	0·4092 (1)	0·2170 (1)	0·2582 (1)	0·041 (0)
P(2)	0·2053 (1)	0·3172 (1)	0·2617 (1)	0·039 (0)
C(123)	0·3253 (4)	0·2470 (4)	0·4711 (4)	0·038 (1)
C(11)	0·2793 (6)	−0·0009 (5)	0·3186 (5)	0·059 (2)
O(11)	0·2347 (5)	−0·0866 (4)	0·2824 (4)	0·099 (2)
C(21)	0·4906 (5)	0·1221 (4)	0·4465 (4)	0·051 (1)
O(21)	0·5802 (4)	0·1185 (4)	0·4883 (4)	0·074 (1)
C(12)	0·0613 (5)	0·1042 (5)	0·3235 (5)	0·059 (2)
O(12)	−0·0125 (5)	0·0328 (4)	0·2892 (4)	0·099 (2)
C(22)	0·1123 (5)	0·3064 (5)	0·4532 (4)	0·057 (2)
O(22)	0·0741 (5)	0·3672 (4)	0·4991 (4)	0·090 (2)
C(13)	0·1899 (6)	0·1964 (6)	0·6291 (5)	0·067 (2)
O(13)	0·1481 (6)	0·2377 (5)	0·6875 (4)	0·111 (2)
C(23)	0·3845 (7)	0·1178 (6)	0·6309 (5)	0·072 (2)
O(23)	0·4626 (5)	0·1102 (5)	0·6916 (4)	0·111 (2)
C(33)	0·1706 (6)	−0·0028 (6)	0·5081 (5)	0·068 (2)
O(33)	0·1137 (5)	−0·0869 (4)	0·4867 (4)	0·101 (2)
C*meth*	0·3585 (4)	0·3440 (4)	0·2554 (4)	0·041 (1)
C(111)	0·3669 (4)	0·1570 (4)	0·1191 (3)	0·048 (1)
C(211)	0·2783 (7)	0·0709 (6)	0·0852 (4)	0·069 (2)
C(311)	0·2468 (8)	0·0259 (7)	−0·0204 (5)	0·092 (3)
C(411)	0·3035 (9)	0·0671 (8)	−0·0900 (4)	0·095 (3)
C(511)	0·3911 (10)	0·1521 (9)	−0·0580 (4)	0·097 (4)
C(611)	0·4235 (7)	0·1977 (7)	0·0473 (3)	0·073 (3)
C(111′)	0·3757 (3)	0·1523 (4)	0·1208 (3)	0·048 (1)
C(211′)	0·3629 (8)	0·0444 (4)	0·0969 (5)	0·070 (2)
C(311′)	0·3375 (10)	−0·0043 (6)	−0·0074 (5)	0·093 (3)
C(411′)	0·3252 (8)	0·0548 (8)	−0·0857 (4)	0·095 (3)
C(511′)	0·3374 (10)	0·1613 (8)	−0·0637 (3)	0·097 (3)
C(611′)	0·3629 (9)	0·2109 (6)	0·0403 (3)	0·073 (3)
C(121)	0·5656 (3)	0·2588 (4)	0·2813 (4)	0·054 (1)
C(221)	0·6273 (4)	0·1907 (4)	0·2442 (5)	0·115 (2)
C(321)	0·7475 (4)	0·2155 (6)	0·2694 (6)	0·159 (3)
C(421)	0·8041 (4)	0·3072 (6)	0·3307 (5)	0·128 (3)
C(521)	0·7447 (4)	0·3754 (5)	0·3680 (5)	0·122 (2)
C(621)	0·6245 (4)	0·3515 (4)	0·3433 (4)	0·093 (2)
C(112)	0·1346 (9)	0·2796 (6)	0·1215 (3)	0·045 (1)
C(212)	0·0596 (13)	0·1842 (9)	0·0863 (6)	0·151 (4)
C(312)	0·0064 (17)	0·1562 (13)	−0·0198 (8)	0·163 (5)
C(412)	0·0287 (21)	0·2233 (15)	−0·0887 (6)	0·082 (5)
C(512)	0·1024 (24)	0·3177 (16)	−0·0554 (5)	0·192 (6)
C(612)	0·1561 (18)	0·3465 (11)	0·0505 (5)	0·169 (4)
C(112′)	0·1267 (9)	0·2647 (8)	0·1257 (4)	0·047 (1)
C(212′)	0·0511 (12)	0·1687 (11)	0·0998 (8)	0·205 (5)
C(312′)	−0·0066 (19)	0·1319 (13)	−0·0041 (9)	0·243 (7)
C(412′)	0·0117 (22)	0·1910 (16)	−0·0801 (7)	0·092 (4)
C(512′)	0·0859 (20)	0·2859 (15)	−0·0560 (6)	0·126 (4)
C(612′)	0·1441 (13)	0·3235 (10)	0·0476 (6)	0·122 (3)
C(122)	0·1755 (3)	0·4530 (3)	0·2857 (3)	0·048 (1)
C(222)	0·0650 (4)	0·4657 (4)	0·2587 (4)	0·080 (1)
C(322)	0·0371 (4)	0·5652 (4)	0·2818 (5)	0·099 (2)
C(422)	0·1191 (5)	0·6500 (4)	0·3311 (4)	0·084 (2)
C(522)	0·2285 (5)	0·6390 (3)	0·3583 (5)	0·105 (2)
C(622)	0·2575 (4)	0·5399 (4)	0·3356 (4)	0·087 (2)

126·2 (3)°]. The bridging asymmetry is rationalized as a mechanism for the dissipation of the electron density built up on the metal triangle by the replacement of the strong π-acceptor carbonyls by the weaker π-acceptor phosphines. It has been suggested that this occurs through the interaction between a carbyne p_π orbital and the t_{2g} orbital of the Co(1)—Co(2) bond (Schilling & Hoffmann, 1978). The other possible mode of relieving the charge build-up due to phosphine substitution is *via* the formation of bridging carbonyl groups. There is no evidence for the formation of bridging or semi-bridging carbonyl groups in the structure of (1).

Table 2. *Bond lengths* (Å) *and selected bond angles* (°) *with their e.s.d.'s for* (μ_3-CCl)Co$_3$(CO)$_7$(μ-dpmm)

Co(2)—Co(1)	2·492 (1)	Co(3)—Co(2)	2·489 (1)
P(1)—Co(1)	2·199 (1)	C(123)—Co(1)	1·857 (5)
C(123)—Co(2)	1·860 (5)	C(123)—Cl	1·772 (5)
C(11)—Co(1)	1·805 (6)	C(21)—Co(1)	1·786 (6)
O(21)—C(21)	1·124 (6)	O(12)—C(12)	1·135 (7)
C(22)—Co(2)	1·765 (6)	C(13)—Co(3)	1·787 (7)
O(13)—C(13)	1·130 (7)	O(23)—C(23)	1·134 (8)
C(33)—Co(3)	1·830 (8)	C*meth*—P(1)	1·835 (5)
C*meth*—P(2)	1·834 (5)	C(111′)—P(1)	1·836 (4)
C(121)—P(1)	1·819 (4)	C(112′)—P(2)	1·839 (4)
C(122)—P(2)	1·841 (4)	C(211)—C(311)	1·391 (3)
C(311)—C(411)	1·335 (4)	O(22)—C(22)	1·146 (7)
Co(3)—Co(1)	2·483 (1)	C(23)—Co(3)	1·788 (7)
P(2)—Co(2)	2·202 (1)	O(33)—C(33)	1·138 (8)
C(123)—Co(3)	1·901 (5)	C(111)—P(1)	1·836 (4)
O(11)—C(11)	1·135 (7)	C(112)—P(2)	1·839 (4)
C(12)—Co(2)	1·807 (6)	C(111)—C(211)	1·354 (3)

Co(2)—Co(1)—Co(3)	60·0 (0)	Co(2)—Co(1)—P(1)	96·7 (0)
Co(2)—Co(1)—C(123)	47·9 (1)	Co(3)—Co(1)—C(123)	49·4 (2)
P(1)—Co(1)—C(123)	101·5 (2)	C(123)—Co(1)—C(11)	141·1 (3)
C(123)—Co(1)—C(21)	101·0 (2)	Co(1)—Co(2)—Co(3)	59·8 (0)
Co(1)—Co(2)—P(2)	95·9 (0)	Co(1)—Co(2)—C(123)	47·9 (1)
Co(3)—Co(2)—C(123)	49·3 (2)	P(2)—Co(2)—C(123)	100·8 (2)
C(123)—Co(2)—C(12)	141·0 (2)	C(123)—Co(2)—C(22)	100·2 (2)
Co(1)—Co(3)—Co(2)	60·2 (0)	Co(1)—Co(3)—C(123)	47·9 (1)
Co(2)—Co(3)—C(123)	47·9 (1)	C(123)—Co(3)—C(13)	104·8 (3)
C(123)—Co(3)—C(23)	101·4 (3)	C(123)—Co(3)—C(33)	140·7 (2)
Co(1)—P(1)—C*meth*	109·4 (2)	Co(2)—P(2)—C*meth*	110·0 (2)
Co(1)—C(123)—Co(2)	84·2 (2)	Co(1)—C(123)—Co(3)	82·7 (2)
Co(2)—C(123)—Co(3)	82·9 (2)	Co(1)—C(123)—Cl	132·0 (3)
Co(2)—C(123)—Cl	131·2 (3)	Co(3)—C(123)—Cl	126·2 (3)
Co(1)—C(11)—O(11)	177·0 (6)	Co(1)—C(21)—O(21)	177·6 (5)
Co(2)—C(12)—O(12)	176·8 (6)	Co(2)—C(22)—O(22)	177·2 (6)
Co(3)—C(13)—O(13)	178·3 (6)	Co(3)—C(23)—O(23)	177·7 (6)
Co(3)—C(33)—O(33)	178·3 (7)	P(1)—C*meth*—P(2)	108·3 (3)

The two axial carbonyls attached to the bridged Co atoms have Co—C_{carbonyl} distances that are identical [Co(1)—C(11) 1·805 (6) and Co(2)—C(12) 1·807 (6) Å] which is in contrast to those found for (2) which are dissimilar at 1·834 (6) and 1·807 (6) Å. The third axial Co—C_{carbonyl} distance in (1) [Co(3)—C(33)] is 1·830 (8) Å which is similar to that in (2) [1·829 (6) Å].

The equatorial Co—C_{carbonyl} distances, Co(3)—C(13), Co(3)—C(23) and Co(1)—C(21), are essentially identical [1·787 (8), 1·788 (8) and 1·786 (6) Å] while the remaining bond, Co(2)—C(22), is slightly shorter [1·765 (6) Å]. In (2) the distances are essentially identical [one is shorter but not significantly so: 1·775 (6)–1·771 (6) Å *versus* 1·763 (6) Å]. The carbonyl C—O bond lengths are all normal and show no remarkable variations. The Co—C—O bond angles are in the range 176·8 (6) to 178·3 (7)°, again as expected and showing no significant structural features.

The dppm ligand bond lengths and angles are similar to those observed for (2), with the comparative values for P(1) and P(2) in (1) showing less variation than in (2). The main variation in the phosphine ligand is in the orientation of the phenyl rings. The two phenyl rings on the same side of the Co triangle as the capping carbyne C atom are both pushed back away from the Cl atom. In (2) one of the phenyl rings appears to be inclined towards the methyl group. In two related structures, (μ_3-CH)$Co_2Mo(CO)_6Cp$(μ-dppm) (Duffy, Kassis & Rae, unpublished) and (μ_3-CH)$Co_2Mn(CO)_8$(μ-dppm) (Duffy, Kassis & Rae, 1990), the upper two phenyl groups are even further inclined toward the apical substituent atom. This indicates a reasonable degree of flexibility in the dppm ligand with the final orientation being controlled by both inter and intramolecular interactions.

The phenyl rings disposed below the metal triangle also display a reasonable degree of flexibility as indicated in (1) by the appearance of disorder in them. The flexibility of the dppm unit and its ability to accommodate steric strain by adopting various configurations is manifest in the position that the methylene C atom adopts in these types of structures. In (1) and the methyl analogue the methylene C atom is in the 'up position'; the unit defined by the carbyne C atom, the two bridged metals and the P—C—P dppm backbone is in a boat configuration. In the two heterometal clusters, (μ_3-CH)-$Co_2Mo(CO)_7Cp$(μ-dppm) (Duffy *et al.*, unpublished) and (μ_3-CH)$Co_2Mn(CO)_8$(μ-dppm) (Duffy *et al.*, 1990), the methylene C atom is in the 'down position', *i.e.* the chair configuration is adopted by the carbyne C atom, the two bridged metals and the P—C—P dppm backbone.

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Structures of Chlorohydroxobis(pentamethylcyclopentadienyl)tantalum(V) Trifluoromethanesulfonate (Triflate) and Dihydroxobis(pentamethylcyclopentadienyl)-tantalum(V) Triflate

BY ROGER W. QUAN, JOHN E. BERCAW AND WILLIAM P. SCHAEFER

Division of Chemistry and Chemical Engineering† *and The Beckman Institute, Mail Code* 139-74, *California Institute of Technology, Pasadena, California* 91125, *USA*

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Abstract. $[Ta(C_{10}H_{15})_2(Cl)(OH)][CF_3SO_3]$ (I), M_r = 652·94, monoclinic, $P2_1/n$, a = 9·965 (7), b = 18·796 (5), c = 13·269 (3) Å, β = 94·02 (3)°, V = 2479·2 (19) Å^3, Z = 4, D_x = 1·75 g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ = 46 cm^{-1}, F(000) = 1288, room temperature, R = 0·107 for 3702 reflections with $F_o^2 > 0$ [R = 0·053 for 2094 reflections with $F_o^2 > 3\sigma(F_o^2)$]. $[Ta(C_{10}H_{15})_2(OH)_2][CF_3SO_3]$ (II), M_r = 634·49, triclinic, $P\bar{1}$, a = 10·052 (2), b = 10·111 (2), c = 12·739 (2) Å, α = 71·38 (2), β = 78·21 (1), γ = 77·40 (2)°, V = 1184·7 (4) Å^3, Z = 2, D_x = 1·78 g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ = 47 cm^{-1}, F(000) = 628, room temperature, R = 0·032 for 4046 reflections with $F_o^2 > 0$ [R = 0·026 for 3664 reflections with $F_o^2 > 3\sigma(F_o^2)$]. Severe disorder of the triflate anion in (I) led to a less satisfactory structure, but cations in both compounds are well defined, with normal Ta—Cp* geometry. Ta—Cl 2·343 (4), Ta—O 1·853 (8) Å and Cl—Ta—O 96·4 (3)° in (I); Ta—O 1·907 (6) Å and O—Ta—O 100·4 (2)° in (II). Tantalum-bound OH groups are hydrogen bonded to triflate O atoms.

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