Supplementary Material (ESI) for Dalton Transactions

Supporting Information for

Electrophilic activation and the formation of an unusual Tl^{+}/Cr^{3+} tetranuclear ion-complex adduct

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Synthesis

General Considerations

All manipulations were carried out under inert argon atmosphere, using standard Schlenk techniques and dried and freshly distilled solvents. Unless otherwise stated, the ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra were recorded on a Bruker Avance 300 instrument at 300.13 and 121.49 MHz, respectively, using TMS or H_3PO_4 (85% in D_2O) as external standards, with downfield shifts reported as positive. All NMR spectra were measured at 298 K, unless otherwise specified. IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer equipped with a Smart Orbit ATR accessory (Ge or diamond crystals). Gas chromatographic analyses were performed on a Thermoquest GC8000 Top Series gas chromatograph using a HP Pona column (50 m, 0.2 mm diameter, 0.5 µm film thickness). Elemental C, H, and N analyses were performed by the Service de microanalyses, Université de Strasbourg (France). The ligand bis(2-picolyl)phenylphosphine (NPN)[S-1] and the complexes $[CrCl_3(THF)_3]$[S-2] and $[CrCl_3(NPN)]\cdot MeCN$[S-3] (Anal. Calcd for $C_{18}H_{17}Cl_3CrN_2P\cdot CH_3CN$: C, 48.85; H, 4.10; N, 8.55. Found: C, 48.69; H, 4.16; N, 8.44) were prepared according to literature procedures. Methylaluminoxane (10 wt % in toluene) was purchased from Sigma-Aldrich.

Crystallographic data

X-ray data collection, structure solution and refinement compounds 1 and 2

For **1**, suitable single crystals for X-ray analysis were grown by layering Et_2O on a concentrated dichloromethane solution of the pure compound and single crystals of **2** by layering Et_2O on a concentrated acetone solution of the pure compound.

The intensity data were collected at 173(2) K on a Kappa CCD diffractometer[S-4] (graphite monochromated MoKa radiation, l = 0.71073 Å). Crystallographic and experimental details for the structures are summarized in Table S1. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (based on F^2, SHELXL-97)[S-5] with anisotropic thermal parameters for all the non-hydrogen atoms. The hydrogen atoms were introduced into the geometrically calculated positions (SHELXS-97 procedures) and refined *riding* on the corresponding parent atoms. CCDC 771851 (**1**) and 771852 (**2**) contain the supplementary crystallographic data for this paper that can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Data collection and refinement parameters for compounds **1** and **2**

Compound	**1**	**2**
Chemical formula	$C_{18}H_{17}Cl_3CrN_2P$	$C_{18}H_{17}Cl_3CrN_2P{\cdot}F_6P{\cdot}Tl$
Formula Mass	450.66	800.00
Crystal system	Monoclinic	Triclinic
a/Å	14.2128(5)	8.9323(4)
b/Å	13.4012(5)	12.0205(5)
c/Å	21.8650(7)	12.8804(4)
α/°	90.00	72.356(2)
β/°	113.705(2)	71.627(2)
γ/°	90.00	69.739(2)
Unit cell volume/Å^3	3813.2(2)	1201.70(8)
Temperature/K	173(2)	173(2)
Space group	$P2_1/c$	P-1
No. of formula units per unit cell, Z	8	2
Absorption coefficient, μ/mm^{-1}	1.108	7.672
No. of reflections measured	15041	9090
No. of independent reflections	8300	5504
R_{int}	0.0608	0.0279
Final R_1 values ($I > 2\sigma(I)$)	0.0483	0.0372
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1057	0.1115
Final R_1 values (all data)	0.1178	0.0469
Final $wR(F^2)$ values (all data)	0.1233	0.1247
Goodness of fit on F^2	0.954	1.088

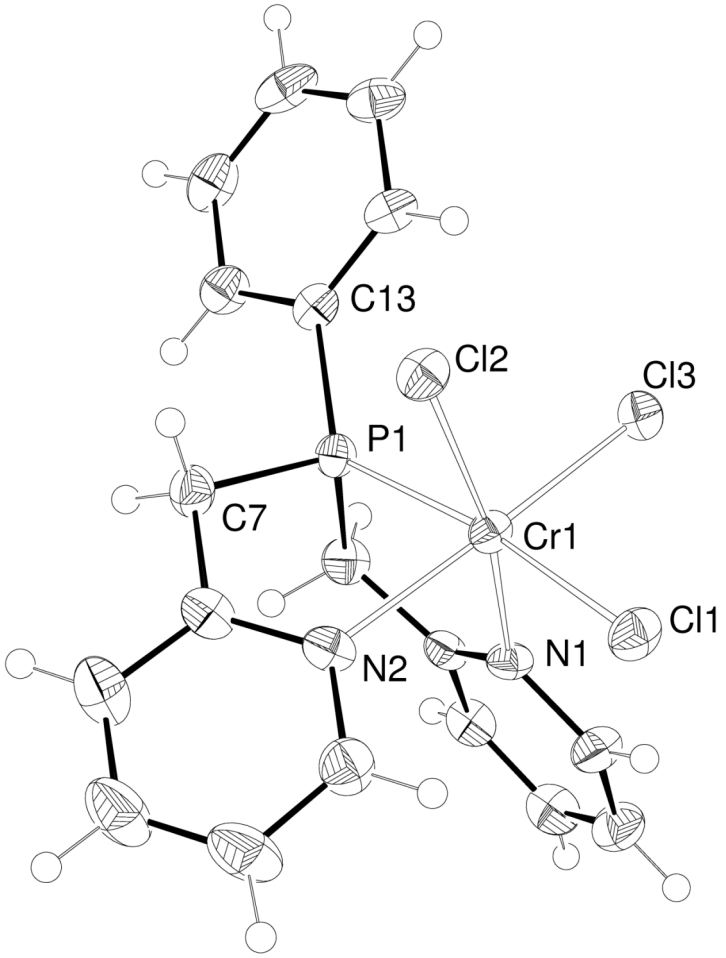

Figure S1. ORTEP view of the molecular structure of **1**. Only one of the two independent molecules is depicted. Ellipsoids are depicted at 50% probability level.

Table S2. Comparison between selected bond distances (Å) and angles (°) between *fac*-[$CrCl_3$(NPN)] in **1** and **2**. In **1**, two crystallographically independent molecules were present.

	1 (molecule A)	**1** (molecule B)	**2**
Cr1-P1	2.351(1)	2.369(1)	2.351(2)
Cr1-N1	2.114(3)	2.137(3)	2.122(5)
Cr1-N2	2.138(3)	2.147(3)	2.124(5)
Cr1-Cl1	2.337(1)	2.320(1)	2.363(2)
Cr1-Cl2	2.315(1)	2.324(1)	2.311(2)
Cr1-Cl3	2.317(1)	2.316(1)	2.328(2)
P1-Cr1-N1	81.89(8)	81.25(9)	80.7(1)
P1-Cr1-N2	78.09(8)	76.41(9)	81.6(1)
N1-Cr1-N2	83.6(1)	88.1(1)	88.7(2)
Cl1-Cr1-Cl2	93.30(4)	94.47(4)	93.04(6)
Cl1-Cr1-Cl3	96.06(4)	93.09(4)	90.86(6)
Cl2-Cr1-Cl3	98.38(4)	95.82(4)	94.03(6)

References

S-1 A. Kermagoret, F. Tomicki and P. Braunstein, *Dalton Trans*., 2008, 2945.

S-2 W. Herwig and H. H. Zeiss, *J. Org. Chem.*, 1958, **23**, 1404.

S-3 K. K. Klausmeyer and F. Hung, *Acta Crystallogr. Sect. E: Struct. Rep. Online*, 2006, **E62**, M2415.

S-4 Bruker-Nonius, *Kappa CCD Reference Manual,* Nonius BV, The Netherlands, **1998**.

S-5 M. Sheldrick, *SHELXL-97*, Program for crystal structure refinement; University of Göttingen: Germany, **1997**.