Preparation and Properties of 1-Adamantylmethyl † and Adamantyl Complexes of Transition Metals ‡

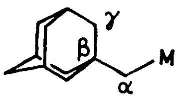
By **Manfred Bochmann, Geoffrey Wilkinson,*** and **G. Brent Young**, Department of Chemistry, Imperial College of Science and Technology, London SW7 2AY

The syntheses and characteristic properties of a variety of 1-adamantylmethyl (R = 1-adme) compounds of transition metals are described. These include peralkyls, MR_n (M = Ti, V, Cr, Mn, or Zr); mixed complexes, MR_nX_m (X = OBu^t or Cl, M = V, Nb, or Ta); π-acid complexes, MR_2L_2 (L = P- or N-donor) including the first example of a thermodynamically favoured *trans*-dialkylplatinum(II) derivative. Additionally, the preparations of bis(1-adamantyl)- and bis(2-adamantyl)-magnesium are reported, as well as successful and inconclusive attempts to produce $Cr(ad)_4$ (ad = 1- or 2-adamantyl).

THE adamantane cage is noted for its inertness towards structural rearrangements.[1] This feature, in addition to its bulk, makes it attractive as a stabilising substituent on transition-metal complexes. Nevertheless, $Ti(1\text{-}ad)_4$ (1-ad = 1-adamantyl) is the only peralkyl transition metal reported [2] so far, although there are a number of examples with non-transition elements.[2,3a,b] There are also a few main-group and transition-metal complexes with additional ligands.[3c,d] We have already reported a variety of alkoxo-derivatives which included adamantyl substituents.[4] We now describe 1-adamantylmethyl and adamantyl complexes.

RESULTS AND DISCUSSION

1-Adamantylmethyl Complexes.—The restriction of the ability of an alkyl transition-metal compound to undergo β-hydride elimination leads to enhanced kinetic stability.[5] It has yet to emerge clearly, however, under which circumstances, and for what reasons, one of the several other rearrangement pathways (α- or ω-hydride migration, reductive elimination, or metal–carbon homolysis) becomes most favourable. Some diamagnetic complexes with neopentyl or trimethylsilylmethyl ligands have, for example, been found to be unstable to γ-hydride elimination.[6] This option should be less available to the related 1-adamantylmethyl compound (I) for two reasons. The vibrational motion of the γ-CH towards the metal, which precedes migration, will be inhibited by the bulk and the interlocked rigidity of the cage. This skeletal inflexibility, moreover, will place considerable strain on any resulting metallacyclobutane ring, which must accommodate a dihedral angle approaching 55° between two of its non-adjacent sides.§ With the view of testing these propositions, and ultimately, of determining which rearrangement(s) may operate, we have synthesised a variety of metal alkyls.



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(*a*) *Peralkyl compounds*, MR_n. These were obtained by transmetallation reactions using precursors in the desired oxidation state,¶ either by (*i*) treatment of a light petroleum-soluble metal alkoxide with Li(1-adme) or (*ii*) interaction in diethyl ether of Li(1-adme) or Mg (1-adme)-Br and a metal halide (1-adme = 1-adamantylmethyl, $C_{10}H_{15}CH_2$). Method (*i*) was particularly suitable for the tetra-alkyls of the first-row metals, whose general insolubility led to clean precipitation of virtually pure products.

Titanium(IV). Addition of $Ti(OPr^i)_4$ to Li(1-adme) in light petroleum at −60 °C affords a yellow solution. After several hours undisturbed at ambient temperature, yellow $Ti(adme)_4$ crystallises in an analytically pure state while the concomitantly formed $LiOPr^i$ remains in solution. This simple procedure may be contrasted with syntheses of $Ti(CH_2CMe_3)_4$ from $TiCl_4$ and $LiCH_2CMe_3$ which are accompanied by extensive decomposition and poorer yields.[7] In fact, preliminary attempts to produce $Ti(adme)_4$ by action of LiR or MgRBr on $TiCl_4$, either in diethyl ether or hydrocarbon solvents, led to analogous deterioration and very low yields. It is worth noting, however, that preparation of the more soluble $Ti(CH_2Ph)_4$ from alkoxide precursors was only moderately successful.[8]

The compound $Ti(adme)_4$ is sparingly soluble in diethyl ether or light petroleum and moderately so in benzene or toluene but it is difficult to recrystallise; decomposition of saturated solutions is visible in 2—3 h at ambient temperature even in the absence of light. Under the same conditions, the solid also will deteriorate gradually, though it may be stored indefinitely at <10 °C. Solutions of $Ti(adme)_4$ are air-sensitive but the solid is sufficiently inert to allow brief handling in air.

Unlike other first-row analogues (see below) $Ti(adme)_4$

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† Tricyclo[3.3.1.1^{3,7}]dec-1-ylmethyl.

‡ No reprints available.

§ Isolable metallacyclobutanes are still rare and structural information is scant. A study of the platinacyclobutane $Pt(CH_2)_3Cl_2(pyridine)_2$ suggests that, although the PtC_3 ring is puckered, the dihedral angle between non-adjacent sides in the equilibrium conformation is *ca.* 10°; R. D. Gillard, M. Keeton, R. Mason, M. F. Pilbrow, and D. R. Russell, *J. Organometallic Chem.*, 1971, **33**, 25.

¶ Syntheses from different oxidation states require intermediate oxidation reduction or disproportionation which generates coupling or H-abstraction products derived from the alkylating agent. The insoluble and involatile adamantylic by-products in this case are more difficulty to separate from the organometallic products.

is soluble enough to allow ^{1}H n.m.r. measurements (Table 1). The significant feature is the high-field singlet (0.81 p.p.m.) due to the α hydrogens. (The cage hydrogens give rise to a second-order spectrum in all adamantylmethyl complexes whose ^{1}H n.m.r. spectra could be measured.)

The i.r. spectrum shows the characteristic twin C–H stretching modes of the adamantyl group near 2 650 cm^{-1} (and also confirms the absence of residual alkoxo-ligands). The complex is insufficiently volatile within the range of its thermal stability to provide a mass spectrum.

Vanadium(IV). While treatment either of VCl_4 or VCl_3O affords only intractable red-grey residues, $V(OPr^i)_4$ reacts with an excess of Li(1-adme) to produce $V(adme)_4$ as fine pale blue crystals. This substance slowly deteriorates at ambient temperature, and decomposes rapidly above 80 °C. The complex is also highly air-sensitive, but may be stored indefinitely at −20 °C under argon. The compound $V(adme)_4$ is, nevertheless, qualitatively more resistant to thermal or aerial destruction than are its closest analogues; $V(CH_2CMe_3)_4$, in contrast, could not be isolated due to its thermal instability above −40 °C;[7] $V(CH_2SiMe_3)_4$, on the other hand, is pyrophoric in air.[9]

TABLE 1

Spectroscopic data for peralkylmetal complexes, R = 1-adme

Complex	Magnetic resonance	I.r. (cm^{-1}) [a]
TiR_4	^{1}H [b]: 0.81 (s, CH_2–Ti), 1.48, 1.70, 1.93 (m, $C_{10}H_{15}$)	2 675w, 2 650w, 1 445vs, 1 370w, 1 352m, 1 344s, 1 308s, 1 290w, 1 273w, 1 204w, 1 185w, 1 137s, 1 122w, 1 096s, 1 074w, 1 057w, 970m, 960w, 933m, 920w, 807m, 777m, 716s, 603s, 515m, 482s, 463m, 420m, 346m, 326m
VR_4	e.s.r. [c]: $g = 1.985$, $\|A_{iso.}\|$ *ca.* 50 G (298 K)	2 675w, 2 650w, 1 446s, 1 375m, 1 342s, 1 307s, 1 286w, 1 270w 1 260w, 1 250w, 1 180w, 1 133s, 1 110m, 1 094s, 1 052m, 1 022m, 970w, 930w, 916w, 803s, 774m, 712s, 600s, 472m, 463m 415m
CrR_4	e.s.r. [d]: $g = 2.004$ (298 K); $g = 1.996$, 4.056 (120 K)	2 900vs, 2 820vs, 2 675w, 2 650s, 1 447s, 1 400w, 1 360w, 1 350m, 1 341s, 1 308s, 1 290w, 1 270w, 1 250m, 1 193w, 1 180m, 1 132m, 1 112m, 1 096m, 1 052s, 1 022s, 986w, 919w, 805ms, 775m, 728w, 712s, 602s, 559m, 532s, 480w, 425w, 331m
MnR_2	e.s.r. [e]: $g = 1.97$ (298 K); $g = 1.98$, 930 G, 1 900 G, 7 700 G (110 K)	2 715w, 2 680w, 1 450vs, 1 368m, 1 343ms, 1 310ms, 1 293m, 1 278w, 1 262w, 1 250w, 1 195w, 1 128m, 1 096s, 1 028s, 972m, 928ms, 920ms, 882w, 810s, 778mw, 728ms, 712s, 585s, 570s, 520m, 507s, 443m, 432m, 333ms
ZrR_4	^{1}H [b]: 0.99 (s, CH_2–Zr), 1.39 (s), 1.46 (m), 1.68 (m), 1.85 (m), 1.95 (br,m) ($C_{10}H_{15}$); ^{13}C [b]: 103.90 (CH$_2$–Zr), 42.51 (CH), 36.80, 28.98 (CH$_2$), 31.79 (CCH$_2$Zr)	2 670w, 2 655w, 1 450vs, 1 360w, 1 345s, 1 310m, 1 302m, 1 190w, 1 134m, 1 096s, 1 025m, 987w, 972m, 958w, 933m, 922w, 880w, 815m, 776w, 713m, 592m, 510w, 475w, 462w, 450w, 425w, 320m

[a] In Nujol mull except CrR_4, recorded as KBr dispersion. Bands obscured by Nujol not listed. [b] In [$^2H_6$]benzene, p.p.m. relative to $SiMe_4$. [c] In toluene. [d] In light petroleum. [e] In benzene.

The poor volatility and thermal stability of $V(adme)_4$ precluded organometallic fragments in the mass spectrum. It is, moreover, too insoluble, even in toluene, at temperatures at which it is stable, to allow either recrystallisation or measurement of ^{1}H n.m.r. spectra. The e.s.r. spectrum of a freshly prepared toluene solution can, however, be observed. The signal, centred on $g = 1.985$, is broadened so that the hyperfine structure is poorly resolved ($|A_{iso.}|$ *ca.* 50 G). The broadening may, conceivably, be the result of suspended solid due to the low solubility of the complex. The i.r. spectrum of $V(adme)_4$ is almost identical to that of its titanium analogue, with which it is presumably isostructural.

Chromium(IV). Addition, in light petroleum, of $Cr(OBu^t)_4$ to an excess of Li(1-adme) yields $Cr(adme)_4$ as a deep maroon, microcrystalline compound. The solid is indefinitely stable at ambient temperature, is unaffected by light, is inert to water, and only slowly attacked by oxygen. Although poorly soluble at ambient temperatures, the complex may be recrystallised without loss from toluene at 80 °C. The solutions are, however, quite air-sensitive.

In light petroleum, at ambient temperature, there is a broad e.s.r. signal centred at $g = 2.004$. Upon cooling to 120 K, the line becomes broader and shifts to $g = 1.996$, while a new sharper, but weaker signal appears at $g = 4.056$. This behaviour may be accommodated assuming a system with $S = 1$ and a small zero-field splitting, which may arise through some distortion from T_d symmetry; the low-field signal is assigned to the nominally forbidden $\Delta M_s = 2$ transition.

The electronic absorption spectrum of a benzene solution shows an intense asymmetric band at 500 nm (ε *ca.* 1 000 dm^3 mol^{-1} cm^{-1}); $Cr(CH_2CMe_3)_4$ has an analogous peak at 473 nm. This may be assigned to the transitions $^3B_1 \rightarrow {}^3E$ (T_1), $B_1 \rightarrow {}^3A_2$ (T_1) for a D_{2d} geometry.[10] The i.r. spectrum resembles those of the Ti and V tetra-alkyls (Table 1).

Manganese(II). $MnBr_2$ reacts readily with two moles of Li(1-adme) in diethyl ether to give an orange-brown solution from which amber, crystalline $Mn(adme)_2$ can be isolated. Toluene solutions of the complex are unaffected by heating up to 70 °C, but are extremely sensitive to traces of oxygen, as is the solid. The magnetic moment of the complex determined in benzene solution by the Evans' paramagnetic-shift method[11] is 3.5 B.M.* This low value cannot be attributed to the antiferromagnetic coupling found in the oligomeric dialkylmanganese compounds,[12] since a cryoscopic

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* Throughout this paper: 1 B.M. = 9.274×10^{-24} A m^2; 1 Torr = (101 325/760) Pa; 1 G = 10^{-4} T; 1 mmHg ≈ 13.6×9.8 Pa.

molecular-weight determination in benzene shows Mn(adme)$_2$ to be monomeric. The e.s.r. spectrum of a benzene solution at ambient temperature comprises a broad symmetric line at $g = 1.97$. On cooling to 83 K, this is replaced by a weaker signal at $g = 1.98$ while a strong unresolved multiplet appears centred at 1 900 G. There is also a moderate band at 930 G and a very weak signal at *ca.* 7 700 G. The spectrum has been compared with those expected from D/B plots and is most compatible with an intermediate spin system of $S = \frac{3}{2}$, with asymmetry parameters D *ca.* 1.0 cm^{-1} and λ $(=E/D)$ *ca.* 0.1. This result is consistent with the observedly low magnetic moment; the spin-only value for $S = \frac{3}{2}$ is 3.87 B.M. Infrared data are listed in Table 1.

Zirconium(IV). Interaction of $ZrCl_4$ with Mg(1-adme)Br in diethyl ether yields a pale yellow solution from which Zr(adme)$_4$ may be recovered as a cream solid. This complex differs appreciably from first-row analogues, especially that of Ti. It is readily soluble in non-polar media and its solutions are thermally inert at ambient temperature. Despite its solubility, however, purification is difficult. As well as acute air-sensitivity, Zr(adme)$_4$ has an affinity for magnesium halide etherate, which persists through successive light petroleum extractions. Halide-free fractions are ultimately difficult to free from 1-methyladamantane.

TABLE 2

Spectroscopic data for vanadium-group complexes MR_nX_m (R = 1-adme)

Complex	Magnetic resonance	I.r. (cm^{-1}) [a]
$VR_2(OBu^t)_2$	e.s.r. [b]: $g = 1.994, \lvert A_{iso.} \rvert = 51$ G (298 K)	2 710w, 2 690w, 2 660w, 1 490w, 1 550vs, 1 424w, 1 390m, 1 360s, 1 312m, 1 236m, 1 225m, 1 190vs, 1 158m, 1 135m, 1 085s, 1 044w, 1 027w, 953vs, 851m, 810m, 770s, 718m, 607vs, 585s, 575s, 510m, 475m, 453m, 436w, 390w, 372s, 355w, 338w, 328w, 295m, 265s
$NbR_2(OBu^t)_3$	^1H [c]: 0.68 (s, CH_2–Nb), 1.38 (s, OBu^t), 1.48, 1.60, 1.80 (m, $C_{10}H_{15}$)	2 675w, 2 655w, 1 450vs, 1 380s 1 357s, 1 343m, 1 310m, 1 260m, 1 230s, 1 204w, 1 178vs, 1 128w, 1 096w, 1 078w, 1 029m, 980vs, 810w, 786s, 712w, 690w, 588m, 540m, 490m, 462w
TaR_3Cl_2	^1H [c]: 2.59 (s, CH_2–Ta), 1.45, 1.68, 1.95 (m, $C_{10}H_{15}$)	2 900vs, 2 850vs, 2 680w, 2 660w, 1 450s, 1 380mw, 1 358ms, 1 345ms, 1 312s, 1 261m, 1 198w, 1 190w, 1 112m, 1 098s, 1 085s, 972w, 920w, 810mw, 715ms, 595ms, 538w, 333s

[a] In Nujol mull, except TaR_3Cl_2, recorded as KBr dispersion. [b] In Toluene. [c] In [$^2H_6$]benzene relative to $SiMe_4$.

The i.r. spectrum is very similar to those of the first-row tetra-alkyls although some bands are less well resolved. The α hydrogens give an ^1H n.m.r. singlet at 0.99 p.p.m. (Table 1). The highest observable fragment in the mass spectrum corresponds to ZrR_3^+.

(*b*) *Complexes of the vanadium group with ancillary anionic ligands:* MR_nX_m. These mainly represent instances of incomplete metathesis of the ligands of the metal presursor.

Vanadium(IV). When V(OBu^t)$_4$ is treated in light petroleum with an excess of Li(1-adme) at low temperature, a deep blue-purple solution results. On warming, dark blue, crystalline V(adme)$_2$(OBu^t)$_2$ separates. This highly air-sensitive compound is only moderately soluble in diethyl ether or light petroleum but dissolves readily in benzene or toluene in which it is monomeric.

The e.s.r. spectrum of a toluene solution shows the eight-line pattern expected for a $S = \frac{1}{2}$ configuration experiencing hyperfine coupling with the ^{51}V nuclear spin $(I = \frac{7}{2})$. The isotropic coupling constant ($\lvert A \rvert = 51$ G) is smaller than that found for V(1-ado)$_4$ ($\lvert A \rvert = 70$ G),[3] consistent with the presence of ligands more covalently bound than alkoxides (1-ado = 1-adamantoxo). The value compares well with that for VMe$_2$(OBu^t)$_2$ ($\lvert A \rvert = 50$ G).[13] The i.r. spectrum has bands characteristic of both adme and OCMe$_3$ groups (Table 2) and a molecular peak is observed in the mass spectrum.

Steric arguments clearly do not explain why all four alkoxo-ligands of V(OBu^t)$_4$ are not displaced as in the chromium analogue. In fact, since Cr^{IV} has the smaller covalent radius, it should by that reasoning be the less substitution labile. If successive methatheses may be regarded as a series of equilibria, then electronic influences must determine the different thermodynamic compatibilities of metal and ligands in the V(adme)$_2$(OBu^t)$_2$ and Cr(adme)$_4$ systems. A different scale of energies, which may also include stereochemical factors, evidently operates for V(OPr^i)$_4$.

Niobium(V). Treatment of Nb(OBu^t)$_4$ with an excess of Li(1-adme) yields a colourless, hydrocarbon-soluble material which appears to be a mixture of di- and tri-alkylated derivatives. Pure diamagnetic Nb(adme)$_2$(OBu^t)$_3$ may be recovered by successive recrystallisations. The crystals and their solutions are air-sensitive, but the solid decomposes thermally only in excess of 200 °C. Spectroscopic data (Table 2) show broad similarities to those for V(adme)$_2$(OBu^t)$_2$.

Tantalum(V). The interaction of $TaCl_5$ with three moles of Mg(1-adme)Br in diethyl ether leads to lemon-yellow needles of Ta(adme)$_3$Cl$_2$. The complex is moderately soluble in aromatic hydrocarbons, in which it is monomeric. The solid is indefinitely stable in air, while solutions are only slowly attacked. The ^1H n.m.r. equivalence of the α hydrogens (2.59 p.p.m.) and the single Ta–Cl i.r. stretching mode (333 cm^{-1}) are consistent with a trigonal-bipyramidal geometry with axial chlorides.

(*c*) *Complexes of the nickel group with π-acid ligands:* MR_2L_2. *Nickel*(II). Treatment of Ni(bipy)Br$_2$ with Li(1-adme) in diethyl ether affords brown-green crystalline Ni(adme)$_2$(bipy) in good yield (bipy = 2,2′-bipyridyl). This appears to be the first instance of a

TABLE 3

Spectroscopic data for nickel-group complexes, MR_2L_2 (R = 1-adme)

Complex	N.m.r. [a]			I.r. (cm^{-1}) [b]
	CH_2–M	1–$C_{10}H_{15}$	L	
NiR_2(bipy)	1.62 (s)	1.78 (m) 2.03 (m)	^{1}H^{c}: 9.62 (d,br; 6 H); 7.80 (m, 3 H and 4 H); 7.52 (m, 5 H)	[d] 3 120vw, 3 100vw, 2 705m, 2 675w, 2 650w, 1 600w, 1 440s, 1 342m, 1 312ms, 1 268m, 1 252m, 1 185m, 1 158m, 1 110m, 1 092m, 1 080w, 1 065w, 1 047w, 1 022w, 1 010m, 982w, 930mw, 815w, 770w, 752vs, 740w, 725s, 650w, 555w, 418w
PdR_2(bipy)	1.79 (s)	1.55 (m) 1.70 (m) 1.40 (m)	^{1}H^{e}: 9.08 (d,br; 6 H); 7.95 (m, 3 H and 4 H); 7.50 (m5, H)	3 120w, 3 100w, 3 070w, 2 900vs, 2 840s, 2 790w, 2 675w, 2 650w, 1 600m, 1 520m, 1 440s, 1 350w, 1 342mw, 1 310m, 1 260w, 1 248m, 1 185w, 1 155mw, 1 105w, 1 093m, 1 075w, 1 063w, 1 043w, 1 022w, 1 012mw, 980w, 930mw, 812mw, 752vs, 735ms, 650w, 628w, 555w, 415
PtR_2(cod)	1.70 [t; ^{2}J(Pt–H) = 90 Hz]	1.62 (d,br) 1.78 (m)	^{1}H^{e}: 4.83 [t,br; ^{2}J(Pt–H) = 38 Hz]; 2.18 [t,br; ^{4}J(Pt–H) *ca.* 16 Hz]	2 900vs, 2 840vs, 2 795w, 2 670w, 2 655w, 1 450s, 1 430w, 1 385w, 1 361w, 1 343s, 1 310m, 1 260m, 1 198w, 1 150mw, 1 098ms, 983w, 970m, 930w, 858w, 812m, 773mw, 755mw, 440vw
$PtR_2(PMe_3)_2$	*f*	1.62 (m) 1.85 (m)	^{1}H^{e}: 1.38 [t of d; ^{2}J(P–H) = 7 Hz; ^{3}J(Pt–H) = 17 Hz; CH_3–P] ^{31}P^{c}: −28.5 [t, ^{1}J(Pt–P) = 1 612 Hz]	2 900vs, 2 840vs, 2 675w, 2 650w, 1 450w, 1 425s, 1 385w, 1 360w, 1 350m, 1 343s, 1 310s, 1 300m, 1 283s, 1 263vs, 1 190w. 1 185w, 1 160w, 1 145w, 1 095s, 957vs, 940vs, 844m, 815m, 718s, 675m, 665m, 403w, 350w
PtR_2(dppm)	1.80 [t of d; ^{2}J(Pt–H) = 80.0 Hz]	1.40 (m) 1.52 (m)	^{1}H^{e}: 7.35, 7.50 (m, H_6C_6–P); 4.14 [t of t, ^{3}J(P–H) = 8.9 Hz; ^{2}J(Pt–H) = 18.7 Hz; H_2C–P]; ^{31}P^{e}: −39.9 [t, ^{1}J(Pt–P) = 1 236 Hz]	3 080mw, 3 060m, 2 900vs, 2 840vs, 2 790m, 2 675w, 2 650w, 1 590w, 1 575w, 1 485s, 1 452s, 1 438vs, 1 388w, 1 362w, 1 350w, 1 344m, 1 312s, 1 257m, 1 190m, 1 100s, 1 085w, 1 030m, 1 002mw, 988w, 975w, 787ms, 741vs 738w, 705w, 693vs, 540s, 505s, 482s, 460w, 430m
$PtR_2(PPh_3)_2$·OEt_2	*f*	1.65 (m) 1.85 (m)	^{1}H^{c}: 6.97, 7.55 (m, H_6C_6–P); ^{31}P^{c}: 27.4 [t, ^{1}J(Pt–P) = 3 438 Hz]	3 080mw, 3 055m, 3 000w, 2 920w, 2 895vs, 2 840s, 2 670w, 2 645w, 1 587w, 1 573w, 1 480s, 1 450mw, 1 432vs, 1 370m, 1 350m, 1 340m, 1 310ms, 1 258mw, 1 190m, 1 155m, 1 120m, 1 090vs, 1 030m, 1 000w, 748m, 736s, 695vs, 534s, 518vs, 511s, 490s, 456m, 420m
PtR_2(bipym)	2.04 [t, ^{2}J(Pt–H) = 92 Hz]	1.46 (m) 1.60 (m)	^{1}H^{e}: 9.77 [t of d, ^{3}J(Pt–H) *ca.* 22 Hz; 6 H]; 9.30 (m, 4 H); 7.62 (t, br, 5 H)	3 080w, 3 040w, 2 900vs, 2 840s, 2 790mw, 2 675w, 2 650w, 1 572ms, 1 547m, 1 469w, 1 448ms, 1 418w, 1 403vs, 1 350m, 1 343mw, 1 310m, 1 262m, 1 195m, 1 150mw, 1 095m,br, 1 013m, 982w, 972w, 933w, 808s, 775w, 750vs, 682w, 662w, 450w, 430w
Pt_2R_4(bipym)	*g*	*g*	*g*	3 130w, 3 080w, 2 900vs, 2 845s, 2 790m, 2 680w, 2 655w, 1 470w, 1 450s, 1 412w, 1 400s, 1 388w, 1 353m, 1 345s, 1 312s, 1 265ms, 1 190s, 1 115m, 1 122w, 1 100m, 1 070w, 1 035w 987w, 975w, 935mw, 803s, 770w, 736s, 560w
$PtR_2(PMePh_2)_2$	*f*	1.53 (m) 1.80 (m)	^{1}H^{e}: H_3C–P^{f}; 7.32, 7.53 (m, H_6C_6–P); ^{31}P^{e}: −3.27 [t, ^{1}J(Pt–P) = 1 658 Hz]	3 080m, 3 055m, 3 000w, 2 985w, 2 900vs, 2 840s, 2 670w, 2 655w, 1 587w, 1 575w, 1 485s, 1 453s, 1 437vs, 1 418w, 1 386mw, 1 345ms, 1 335w, 1 310s, 1 288m, 1 275w, 1 255m, 1 188ms, 1 160w, 1 146m, 1 096s, 1 075w, 1 030m, 1 000w, 975w, 878vs, 818mw, 752s, 738vs, 730w, 697vs, 680w, 620w, 610w, 518vs, 478m, 422ms, 410ms, 320w
PtR_2(bipy)	1.98 [t, ^{2}J(Pt–H) = 88 Hz]	1.50 (m) 1.68 (m)	^{1}H^{e}: 9.62 [t of d, ^{3}J(Pt–H) *ca.* 24 Hz; 6 H]; 8.00 (m, 3 H and 4 H); 7.53 (m, 5 H)	3 120w, 3 100w, 3 080w, 2 900vs, 2 840s, 2 785w, 2 670w, 2 650w, 1 600w, 1 469m, 1 443s, 1 400m, 1 387mw, 1 350w, 1 342w, 1 310m, 1 260w, 1 200w, 1 155w, 1 100w, 1 093w, 1 080w, 983w, 933w, 810w, 752vs, 730s, 630w, 420w

[a] ^{1}H, p.p.m. relative to $SiMe_4$. ^{31}P p.p.m. relative to external 60% H_3PO_4; downfield shifts positive. [b] Recorded in 5% KBr dispersion unless otherwise specified. [c] In [$^{2}H_6$]benzene. [d] Nujol mull. [e] In [$^{2}H_1$]chloroform. [f] Obscured. [g] Insufficiently soluble.

useful synthesis of Ni(bipy)R_2 by direct transmetallation on the halide; previous examples have required the action of bipy and organoaluminium agents on Ni(acac)$_2$,[14a] or oxidative additions to Ni(bipy)(cod) (acac = pentane-2,4-dionate, cod = cyclo-octa-1,5-diene).[14b] Diamagnetic Ni(adme)$_2$(bipy) has sufficient thermal stability to allow recrystallisation from hot toluene, but its intense green solutions are highly air-sensitive. The solid and its solutions are hydrolytically inert. The i.r. and ^{1}H n.m.r. spectra have bands for both 2,2′-bipyridyl and 1-adme ligands (Table 3).

Palladium(II). Interaction of Pd(bipy)Br_2 and Li(1-adme) yields diamagnetic Pd(adme)$_2$(bipy) as fine scarlet needles. Like its nickel and platinum analogues, it is poorly soluble, but may be recovered from hot acetone. The solid is air-stable, but solutions deteriorate rapidly. Neither are affected by degassed water. One previous example of PdR_2(bipy) has been reported (R = Me).[15]

Platinum(II). Addition of Mg(1-adme)Br to PtCl_2(cod), followed by low-temperature chromatography,[16] gives efficient conversion to Pt(adme)$_2$(cod). The yellow-white crystals are inert to air, water, or light [as are subsequently described platinum(II) derivatives]. Although thermally stable, its solutions in protic media (alcohols) slowly decompose at room temperature. The diene ligand is readily displaced by other donors and Pt(adme)$_2$(cod) is the precursor to other PtR_2L_2 complexes discussed below.

Spin–spin coupling of neighbouring nuclei with ^{195}Pt (33.8%; $I = \frac{1}{2}$) gives a characteristic 1 : 4 : 1 pattern to their n.m.r. signals. In the ^{1}H n.m.r. spectrum of Pt(adme)$_4$(cod), the significant J values are those for the olefinic hydrogens on the diene [^2J(Pt–H) = 38 Hz] and the α hydrogens of the alkyl [^2J(Pt–H) = 90 Hz]. These typical values [*cf.* those for PtMe_2(cod) of 40 Hz and 86 Hz respectively [17]] confirm the identity of the complex and suggest no unusual steric or electronic impositions by the 1-adme substituent in this molecule.

The compound Pt(adme)$_2$(cod) reacts smoothly with PMe_3 to generate *cis*-Pt(adme)$_2$(PMe_3)$_2$ as colourless, diamagnetic, air-stable prisms. The *cis* configuration is confirmed both by the absence of ' virtual ' J(P–H) coupling [18] in the ^{1}H n.m.r. and by the value ^1J(Pt–P) = 1 612 Hz from the ^{31}P n.m.r. spectrum. This value, although slightly lower than expected, is characteristic of a Pt–P bond *trans* to a ligand of high n.m.r. *trans* influence [such as an alkyl; *cf.* *cis*-PtMe_2(PEt_3)$_2$: ^1J(Pt–P) = 1 856 Hz [19]]. The decrease may reflect some geometric distortion as a result of the large, inflexible alkyl groups.

When treated with bis(diphenylphosphino)methane (dppm), Pt(adme)$_2$(cod) is converted quantitatively to Pt(adme)$_2$(dppm). A *cis* geometry is required for this bidentate ligand in mononuclear complexes. Hydrogen-1 and ^{31}P n.m.r. data (Table 3) indicate spin–spin coupling to a single ^{195}Pt nucleus, confirming chelation by dppm. The value of ^1J(Pt–P) = 1 236 Hz is very low for complexes of the type *cis*-PtR_2P_2. Anomalously low values have previously been noted in dppm derivatives; *e.g.* for PtMe_2(dppm) [^1J(Pt–P) = 1 424 Hz] and PtPh_2(dppm) [^1J(Pt–P) = 1 391 Hz].[20] A structural examination of the diphenyl complex showed that the abnormality may be ascribed to severe angular distortions about P and Pt, imposed by the four-membered ring.[20a] In Pt(adme)$_2$(dppm), however, the value is significantly lower. (In fact, it falls within the range more normally encountered for phosphine *trans* to alkyl in Pt^{IV} species.) Clearly, there are additional molecular distortions, perhaps due to the encroachment of the bulky alkyl groups upon the aryl substituents on phosphorus.

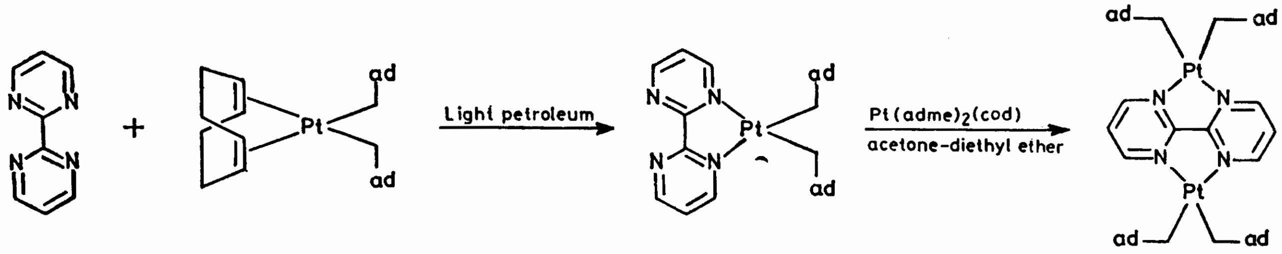
Interaction of PPh_3 and Pt(adme)$_2$(cod) gives poorly soluble diamagnetic yellow crystals of Pt(adme)$_2$(PPh_3)$_2$·solvent (solvent = dichloromethane or diethyl ether, depending on recrystallisation). The ^{31}P n.m.r. spectrum shows ^1J(Pt–P) = 3 438 Hz, which indicates a *trans* configuration for the molecule. This, presumably, is the result of unfavourable steric interactions between the bulky adamantyl ligands and the spatially demanding phosphines. Hydrogen-1 n.m.r. indicates that the occluded solvent molecules do not interact with the complex in solution.

Apart from the rather poorly characterised *trans*-PtMe_2(PEt_3)$_2$,[21] this is the only example of a *trans*-dialkylplatinum(II) compound and is certainly the first example for which the *trans* configuration is thermodynamically favoured. An X-ray diffraction study is in progress, and the molecular dimensions may also provide an explanation of the high value of ^1J(Pt–P), which is abnormal even for *trans* phosphines [*cf.* *trans*-PtPh_2(PEt_3)$_2$: ^1J(Pt–P) = 2 824 Hz; *trans*-PtCl_2(PPh_3)$_2$: ^1J(Pt–P) = 2 655 Hz [22]].

Unidentate $PMePh_2$ is sterically and electronically intermediate between dppm and PPh_3. It displaces cod readily from Pt(adme)$_2$(cod) to yield Pt(adme)$_2$($PMePh_2$)$_2$ as colourless crystals. Although the value of ^1J(Pt–P) = 1 658 Hz is again lower than might be expected [*cf.* *cis*-PtMe_2($PMePh_2$)$_2$: ^1J(Pt–P) = 1 851 Hz [20b]] the less cluttered phosphine obviously allows adoption of the *cis* geometry.

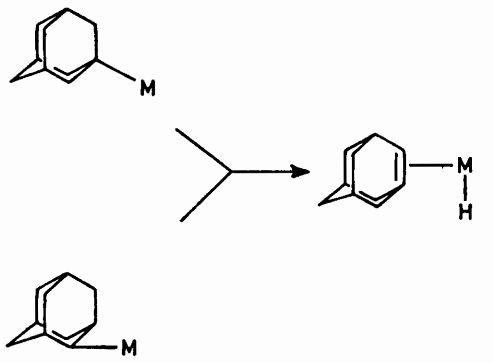
In order to establish a homologous series of nickel palladium, and platinum complexes, for subsequent comparative studies, Pt(adme)$_2$(cod) was treated with 2,2′-bipyridyl, giving Pt(adme)$_2$(bipy) as fine, purple-maroon needles. In contrast with its nickel and palladium analogues, this compound is notably stable and will survive several hours reflux in acetone under air without deterioration.

Very few complexes of the related species 2,2′-bipyrimidyl (bipym) have previously been reported. This ligand has the capacity to act as a bidentate ligand either to a single or to two metal nuclei.[23] Reaction of 2,2′-bipyrimidyl with Pt(adme)$_2$(cod) in light petroleum leads to separation of red-grey crystals established to be Pt(adme)$_2$(bipym). In particular, the i.r. spectrum has bands at 1 545 and 1 570 cm^{-1} indicating an unco-ordinated C=N unit. Treatment of Pt(adme)$_2$(bipym) in acetone with one equivalent of Pt(adme)$_2$(cod) in diethyl ether gives fine brown-green crystals of (adme)$_2$-Pt(bipym)Pt(adme)$_2$. The identity of the dinuclear complex is confirmed by its spectroscopic properties and its molecular weight (Tables 3 and 4). Major features of these reactions are summarised in Scheme 1.



SCHEME 1

Adamantyl Complexes.—The unfavourability of cage-bridgehead alkenes and, probably, their high steric demand explain the remarkable stability of peralkyl transition-metal complexes of the bicyclo[2.2.1]hept-1-yl ligand.[24] The 1-adamantyl group is analogous, but only Ti(1-ad)$_4$ has been reported, although several non-transition-metal derivatives are known.[2,3] Since β-elimination from a 2-adamantyl metal complex would generate the same disfavoured adamantene (Scheme 2), these should also be a relatively inert class of organometallics.



SCHEME 2

The compound Mg(2-ad)Br (2-ad = 2-adamantyl) may be prepared by reaction of the halide with a large excess of magnesium, in similar fashion to Mg(1-adme)Br. Reaction of this Grignard reagent with metal halides has led to disappointing results. With PtCl$_2$(cod) only 2,2′-biadamantyl was recovered. Reaction with CrCl$_3$-(thf)$_3$ (thf = tetrahydrofuran) in diethyl ether affords an homogeneous blue-purple solution. The species responsible, presumably the anion [Cr(2-ad)$_4$]$^-$, from its colour and e.s.r. spectrum,[9] is stable only in diethyl ether. Attempts to isolate or oxidise it led only to decomposition.

The dialkylmetal Mg(2-ad)$_2$ may be obtained diethyl ether-free *via* the Grignard by displacement of the Schlenck equilibrium.[25] When a light petroleum suspension of this reagent is treated with Cr(OBu^t)$_4$, maroon-brown crystals of Cr(2-ad)$_4$ are obtained in low yield. The solid is air-stable and poorly soluble. It may be recrystallised from hot toluene in which it is slowly attacked by air.

The compound Mg(1-ad)Br is also accessible.[3b] Treat-

TABLE 4

Analytical data

Compound	M.p. (θ_c/°C)	Found [a]					Required [a]				
		C	H	N	Other	*M*	C	H	N	Other	*M* [b]
Ti(adme)$_4$	145 [c]	80.3	10.5				82.0	10.6			
V(adme)$_4$	80 [c]	78.7	10.3				81.6	10.6			
Cr(adme)$_4$	164 [c]	80.75	10.4				81.45	10.55			
Mn(adme)$_2$	187 [d]	73.8	9.65			340 [e]	74.75	9.7			353
Zr(adme)$_4$	130 [c]	79.6	10.5				76.8	10.0			
V(adme)$_2$(OBu^t)$_2$	130 [c]	71.6	10.8		O: 7.1	420 [e]	72.7	10.3		O: 6.5	496
Nb(adme)$_2$(OBu^t)$_3$	250 [c]	65.6	9.9				66.8	10.0			
Ta(adme)$_3$Cl$_2$	180 [c]	55.9	7.2		Cl: 9.75	686 [e]	56.65	7.25		Cl: 10.15	700
Ni(adme)$_2$(bipy)	178 [d]	75.0	8.25	5.45			74.85	8.25	5.4		
Pd(adme)$_2$(bipy)	160 [c]	67.7	7.5	4.95			68.5	7.55	5.0		
Pt(adme)$_2$(cod)	161 [d]	59.85	7.75				59.85	7.7			
Pt(adme)$_2$(PMe$_3$)$_2$	128 [d]	51.95	8.1				52.1	8.1			
Pt(adme)$_2$(dppm)	245 [d]	64.35	6.4				64.3	6.45			
Pt(adme)$_2$(PPh$_3$)$_2$·OEt$_2$	138 [d]	68.3	6.9				68.05	6.8			
Pt(adme)$_2$(PMePh$_2$)$_2$	164 [d]	64.4	6.75				64.35	7.0			
Pt(adme)$_2$(bipy)	165 [c]	59.05	6.55	4.15			59.15	6.5	4.3		
Pt(adme)$_2$(bipym)	180 [c]	55.5	6.3	8.45		638 [f]	55.3	6.15	8.6		651
Pt$_2$(adme)$_4$(bipym)	220 [c]	54.45	5.55	5.1		1 115 [f]	55.0	5.7	4.95		1 135
Mg(1-ad)$_2$·2OEt$_2$	188 [d]	70.85	12.4		O: 7.8		73.0	12.75		O: 8.1	
Cr(2-ad)$_4$	125 [c]	80.35	10.1				81.05	10.2			

[a] Values of C,H,N, and other in percentages. [b] Monomeric. [c] Decomposes without melting. [d] With decomposition. [e] Cryoscopically in benzene. [f] Osmometrically in dichloromethane.

ment of $PtCl_2(cod)$ with this agent affords 1,1′-biadamantyl. The preparation of diethyl ether-free $Mg(1\text{-}ad)_2$ is analogous. Interaction of the dialkyl with $Cr(OBu^t)_4$ or with $Cr(OCHBu^t{}_2)_4$ [26] gives a red-brown, highly insoluble product. The colour is similar to those of the other chromium(IV) alkyls and the very simple i.r. spectrum indicates the presence only of adamantylic species. The data are thus far in accord with the presence of $Cr(1\text{-}ad)_4$. On the other hand, although the product may be obtained as fine red-brown crystals by several weeks' extraction into thf, satisfactory elemental analyses have not been obtained. Whereas the very low solubility of the material is in harmony with our observations on $Cr(adme)_4$ and $Cr(2\text{-}ad)_4$, it differs from the reported behaviour of $Ti(1\text{-}ad)_4$.[2]

Reaction of $Mg(1\text{-}ad)_2$ with $TiCl_4$, $Ti(OPr^i)_4$, or $MnBr_2$ has not led to tractable organometallic products.

EXPERIMENTAL

Microanalyses were by Pascher and by Butterworth Laboratories. Spectroscopic measurements were performed on Perkin-Elmer R 32 (^1H n.m.r., 90 MHz); Varian XL-100 (^{31}P and ^{13}C n.m.r.); Varian E12 (*X*-band e.s.r.); Perkin-Elmer 457 (i.r.); and VG Micromass (mass spectroscopy). Solvents for anaerobic manipulations were distilled under nitrogen; diethyl ether and tetrahydrofuran from sodium benzophenone dianion, light petroleum (b.p. 40—60 °C) and benzene from sodium benzophenone ketyl, and toluene and 1,4-dioxan from sodium. Except for platinum complexes, melting points were determined in evacuated capillaries, all uncorrected. 1-Adamantylmethanol, 1- and 2-bromoadamantane were used as supplied (Aldrich Chemical Co.). 2% Sodium lithium alloy was obtained as a dispersion in oil (Alfa). 2,2′-Bipyrimidyl was supplied by Lancaster Syntheses Ltd. Analytical details for all new compounds are tabulated (Table 4).

1-*Bromomethyladamantane*.—This compound was prepared by modifying established procedure.[27] 1-Adamantylmethanol (20 g, 120 mmol), $ZnBr_2$ (40 g, 180 mmol), and aqueous 48% HBr (30 cm^3, *ca.* 180 mmol) were refluxed together (110 °C) for 45 min. Upon cooling, the alkyl bromide crystallised as a crust. The aqueous phase was decanted, the product washed, extracted into diethyl ether, dried, and sublimed (70 °C, 0.1 Torr) to yield pure 1-bromomethyladamantane (26 g, 95%).

1-*Bromomagnesiomethyladamantane*.[28]—To a stirred suspension of flamed magnesium turnings (1.47 g, 60.44 mg-atom) in diethyl ether (60 cm^3) at ambient temperature under argon was added dropwise a solution of 1-bromomethyladamantane (2.32 g, 10.12 mmol) in the same solvent (80 cm^3). Addition took 6 h. After 0.5 h stirring, the colourless supernatant was filtered off. A sample was quenched with distilled water and the resultant solution titrated against 0.1 mol dm^{-3} HCl. The concentration of Mg(1-adme)Br was estimated to be 0.06 mol dm^{-3} (135 mol, 75% based on RBr).

1-*Lithiomethyladamantane*.—A fine dispersion of lithium containing 2% sodium (2.0 g, 288 mg-atom) and broken glass were suspended together in diethyl ether (100 cm^3) under argon. The mixture was stirred vigorously and cooled to 0 °C. To the suspension was added dropwise, over at least 4 h, a solution of 1-bromomethyladamantane (4.00 g, 17.46 mmol) in the same solvent (80 cm^3). After addition, the mixture was allowed to reach ambient temperature and the colourless or slightly yellow supernatant was filtered off. The organolithium concentration was determined by a modification of the double titration method of Gilman *et al.*[29]; separate aliquots were quenched with water, and successively with 1,2-dibromoethane and water, and titrated against 0.1 mol dm^{-3} HCl.

Yields in this reaction are extremely sensitive to reaction conditions; impure materials, higher temperatures, rapid addition, insufficient agitation, or absence of broken glass may all lead to inferior results. Yields of 65—80% have, however, been reliably achieved using this procedure. The compound Li(1-adme) slowly decomposes in diethyl ether, even at −30 °C, but is indefinitely stable in light petroleum (in which it is readily soluble).

Tetrakis(1-*adamantylmethyl*)*titanium*(IV).—To a stirred solution of Li(1-adme) (5.2 mmol) in light petroleum (40 cm^3) at −20 °C was slowly added a solution of $Ti(OPr^i)_4$ [30] (0.30 g, 1.06 mmol) in the same solvent (5 cm^3). Stirring was stopped after thorough mixing, the solution was allowed to reach ambient temperature and allowed to stand for 3 h. The resulting lemon crystals of $Ti(adme)_4$ were filtered off and dried (0.40 g, 60%).

Tetrakis(1-*adamantylmethyl*)*vanadium*(IV).—A light petroleum solution (10 cm^3) of $V(OPr^i)_4$ [31] (1 mmol) was added dropwise to a stirred solution of Li(1-adme) (5.0 mmol) in light petroleum (40 cm^3) at −60 °C. The grey-green mixture was allowed to attain 0 °C, the blue-green microcrystalline $V(adme)_4$ was collected at this temperature and thoroughly dried (0.35 g, 54%).

Bis(1-*adamantylmethyl*)*bis*(*t-butoxo*)*vanadium*(IV).— A light petroleum solution (10 cm^3) of $V(OBu^t)_4$ [31] (1 mmol) was slowly added to Li(1-adme) (5 mmol) in the same solvent (40 cm^3) at −50 °C. A deep blue-purple solution results. Upon warming to ambient temperature, dark blue crystals of $V(adme)_2(OBu^t)_2$ separated. These were recrystallised from toluene (0.30 g, 60%).

Tetrakis(1-*adamantylmethyl*)*chromium*(IV).—To a stirred solution of Li(1-adme) (6.6 mmol) in light petroleum (45 cm^3) at −60 °C was slowly added a light petroleum solution (45 cm^3) of $Cr(OBu^t)_4$ [32] (1.08 mmol). The solution became maroon as addition proceeded and dark maroon crystals were deposited. The mixture was allowed to reach ambient temperature and stirred for 0.5 h. The insoluble $Cr(adme)_4$ was filtered off and recrystallised from hot (80 °C) toluene (0.46 g, 45%).

Bis(1-*adamantylmethyl*)*manganese*(II).—A freshly prepared solution of Li(1-adme) (14.0 mmol) in diethyl ether (200 cm^3) was rapidly added, at ambient temperature, to stirred anhydrous $MnBr_2$ (1.54 g, 7.0 mmol). The mixture was protected from light and stirred for 16 h. The solvent was then distilled out (30 mmHg) and the tan residue thoroughly dried. Toluene was added (40 cm^3) and the pale brown supernatant filtered off, concentrated (to *ca.* 15 cm^3) *in vacuo*, and stored at −30 °C. Fine amber plates of $Mn(adme)_2$ separated (1.36 g, 55%).

Tetrakis(1-*adamantylmethyl*)*zirconium*(IV).—To a stirred suspension of $ZrCl_4$ (0.70 g, 3.0 mmol) in diethyl ether (20 cm^3 at −50 °C) was added Mg(1-adme)Br (13 mmol) in the same solvent (80 cm^3). The mixture was stirred at ambient temperature for 16 h and filtered. The supernatant solvent was evaporated and the residue extracted with light petroleum (3 × 20 cm^3). The light petroleum was concentrated, cooled (−20 °C), and centrifuged several times to remove magnesium halide etherate, which persisted. A cream-coloured solid was finally obtained (0.80 g, 39%).

Bis(1-*adamantylmethyl*)*tris*(*t-butoxo*)*niobium*(V).— Upon addition of $Nb(OBu^t)_5$ [33] (1.0 mmol) to Li(1-adme) (5.5 mmol) in light petroleum (40 cm^3) at −60 °C, a colourless solution was obtained which was stirred at ambient temperature for 1 h. The liquor was concentrated by evaporation and cooled to −30 °C to afford fine white crystals. These were twice recrystallised from diethyl ether (0.09 g, 15%).

Tris(1-*adamantylmethyl*)*dichlorotantalum*(V).—To a stirred solution of $TaCl_5$ (0.93 g, 2.60 mmol) in diethyl ether (90 cm^3) at −50 °C was added a solution of Mg(1-adme)Br (7.98 mmol) in the same solvent (145 cm^3). The mixture was finally stirred at ambient temperature for 2 h. The supernatant became successively greenish yellow, golden, and bronze. The solvent was removed *in vacuo* and toluene (25 cm^3) added. The golden liquors were filtered, concentrated (to *ca.* 10 cm^3), and cooled (−30 °C) to give a pale yellow powder. Two further recrystallisations from toluene yielded lemon-yellow filamentous needles of $Ta(adme)_3Cl_2$ (0.55 g, 30%).

Bis(1-*adamantylmethyl*)(2,2′-*bipyridyl*)*nickel*(II).—To a stirred suspension of $Ni(bipy)Br_2$ [34] (0.73 g, 1.95 mmol) in diethyl ether (10 cm^3) at −75 °C was rapidly added a solution of Li(1-adme) (3.9 mmol) in the same solvent (65 cm^3), also at −75 °C. The deep bottle-green solution was stirred at −30 °C for 4 h until all of the starting material had dissolved. The supernatant was filtered at ambient temperature, and the diethyl ether evaporated, leaving a grey-green solid. The original reaction residue, meanwhile, was treated with warm (40 °C) toluene (45 cm^3) and the resulting dark green solution was filtered, concentrated *in vacuo*, and cooled to −30 °C. Fine brown-green crystals of $Ni(adme)_2(bipy)$ separated (0.68 g, 68%). Similar treatment of the diethyl ether residue gave a small additional amount of the product.

Bis(1-*adamantylmethyl*)(2,2′-*bipyridyl*)*palladium*(II).— To a stirred suspension of $Pd(bipy)Br_2$ [35] (0.83 g, 1.96 mmol) in diethyl ether (20 cm^3) at −70 °C was slowly introduced a solution of Li(1-adme) (5.0 mmol) in diethyl ether (50 cm^3). The mixture was allowed to reach room temperature, and was stirred for 1 h. The pale brown-red supernatant was filtered off and the residue was treated with deoxygenated acetone (50 cm^3) at 50 °C. The rich red supernatant was filtered and cooled first to 0 °C for 16 h and then to −30 °C. Fine scarlet needles of $Pd(adme)_2(bipy)$ were obtained (0.52 g, 47%).

Bis(1-*adamantylmethyl*)(*cyclo-octa*-1,5-*diene*)*platinum*(II). —To a stirred suspension of $PtCl_2(cod)$ [36] (0.50 g, 1.34 mmol) in diethyl ether (25 cm^3) at −40 °C was slowly added Mg(1-adme)Br (3.25 mmol) in the same solvent (65 cm^3). The mixture was allowed to reach 0 °C and was stirred for 4 h. The pale amber supernatant was eluted on a column of charcoal–silica gel [16] maintained at 0 °C under argon. The residue was washed with portions of fresh diethyl ether (3 × 10 cm^3) which were also passed through the adsorbent. The solvent was then pumped off and the sticky amber residue was dissolved in the minimum volume of diethyl ether, an equivalent volume of methanol added, and the mixture cooled to yield yellow-white crystals (0.70 g, 87%). (Anaerobic handling was unnecessary after chromatography.)

Bis(1-*adamantylmethyl*)(2,2′-*bipyridyl*)*platinum*(II).—2,2′-Bipyridyl (0.15 g, 0.96 mmol) dissolved in light petroleum (10 cm^3) was added to a solution of $Pt(adme)_2(cod)$ (0.53 g' 0.88 mmol), in the same solvent (15 cm^3), giving a wine-red solution. During 60 h at ambient temperature there was copious precipitation of dark purple-crimson crystals of $Pt(adme)_2(bipy)$ in an analytically pure state (0.51 g, 89%).

cis-*Bis*(1-*adamantylmethyl*)*bis*(*trimethylphosphine*)*platinum*(II).—To a stirred solution of $Pt(adme)_2(cod)$ (0.51 g, 0.85 mmol) in diethyl ether (10 cm^3) at 0 °C was added dropwise a solution of PMe_3 (0.15 g, 0.95 mmol) in the same solvent (10 cm^3). The solution was stored at 0 °C for 16 h after which the solvent was removed *in vacuo* leaving a white residue. This material was twice recrystallised from diethyl ether–methanol (1 : 1) to give fine white plates of $Pt(adme)_2(PMe_3)_2$.

Bis(1-*adamantylmethyl*)*bis*(*diphenylphosphino*)*methaneplatinum*(II).—$Pt(adme)_2(cod)$ (0.22 g, 0.37 mmol) and dppm (0.15 g, 0.39 mmol) were dissolved together in diethyl ether (15 cm^3). The mixture was stirred at ambient temperature for 18 h. The resulting ivory precipitate was filtered off and recrystallised from methylene chloride–methanol (1 : 1) to give large prisms (0.29 g, 88%).

trans-*Bis*(1-*adamantylmethyl*)*bis*(*triphenylphosphine*)-*platinum*(II).—$Pt(adme)_2(cod)$ (0.50 g, 0.83 mmol) and PPh_3 (0.48 g, 1.83 mmol) were dissolved together in diethyl ether (20 cm^3). The solution was allowed to stand at ambient temperature in darkness for 30 h. Evaporation of solvent left a pale yellow fluid which crystallised on trituration with diethyl ether. The solid was recrystallised from methylene chloride–methanol (1 : 1) yielding pale greenish-yellow plates of $Pt(adme)_2(PPh_3)_2{\cdot}CH_2Cl_2$ (0.78 g, 85%). Alternatively, recrystallisation from diethyl ether afforded pale yellow prisms of $Pt(adme)_2(PPh_3)_2{\cdot}OEt_2$.

cis-*Bis*(1-*adamantylmethyl*)*bis*(*methyldiphenylphosphine*)-*platinum*(II).—Neat $PMePh_2$ (0.24 g, 1.20 mmol) was slowly added to a solution of $Pt(adme)_2(cod)$ (0.31 g, 0.52 mmol) in diethyl ether (15 cm^3) at 0 °C. The solution was allowed to remain at ambient temperature for 16 h. The solvent was evaporated and the yellow-white residue was recrystallised from methylene chloride–methanol to yield colourless prisms of $Pt(adme)_2(PMePh_2)_2$ (0.40 g, 86%).

Bis(1-*adamantylmethyl*)(2,2′-*bipyrimidyl*)*platinum*(II).— To a stirred suspension of 2,2′-bipyrimidyl (0.07 g, 0.42 mmol) in light petroleum (30 cm^3) at ambient temperature was added $Pt(adme)_2(cod)$ (0.27 g, 0.45 mmol) in the same solvent (15 cm^3). The mixture was stirred for 60 h during which the solution became red and finally green. The supernatant was filtered off and the residue extracted into acetone. The deep red solution was concentrated and cooled to afford fine grey-red crystals of $Pt(adme)_2(bipym)$ (0.24 g, 86%). This was also the product when a two-fold excess of $PtR_2(cod)$ was used in this solvent.

Tetrakis(1-*adamantylmethyl*)(2,2′-*bipyrimidyl*)*diplatinum*-(II).—A solution of $Pt(adme)_2(cod)$ (0.15 g, 0.26 mmol) in diethyl ether (15 cm^3) was added to $Pt(adme)_2(bipym)$ (0.15 g, 0.23 mmol) dissolved in acetone (15 cm^3). Over 7 days at ambient temperature, brownish green prisms of $(adme)_2Pt(bipym)Pt(adme)_2$ separated. These were recrystallised from methylene chloride (0.21 g, 80%).

Bis(2-*adamantyl*)*magnesium*.—To a stirred suspension of flamed magnesium turnings (1.91 g, 78.6 mg-atom) in diethyl ether (70 cm^3) was added, over 3 h, a solution of 2-bromoadamantane (3.35 g, 15.57 mmol) in the same solvent (80 cm^3). 1,2-Dibromoethane (0.15 cm^3) was introduced as an initiator. The mixture was stirred for 4 h after addition and the solvent was reduced by evaporation (to 90 cm^3).

The supernatant was filtered off into an argon-flushed 200-cm^3 centrifuge flask. Analysis showed the concentration of $\mathrm{Mg(2\text{-}ad)Br}$ to be 0.01 mol dm^{-3} (60% yield). Neat 1,4-dioxan (1.7 cm^3) was added slowly with vigorous stirring. The chalky suspension was stirred for 6 h. The solid was then compacted by centrifugation and the supernatant filtered off. The solvent was distilled out *in vacuo* and 2,2′-biadamantyl and traces of dioxan were removed from the white solid product by heating at 120 °C (10^{-2} Torr) for 20 h. The solid, now halide free, was redissolved in diethyl ether for use without further characterisation or purification. It is only slightly soluble in hydrocarbons. (Analysis indicated an overall yield of 54% based on 2-bromoadamantane.)

Tetrakis(2-*adamantyl*)*chromium*(IV).—To a stirred suspension of $\mathrm{Mg(2\text{-}ad)_2}$ (0.83 g, 2.8 mmol) in light petroleum (60 cm^3) at −10 °C was added dropwise (over 1 h) a light petroleum solution of $\mathrm{Cr(OBu^t)_4}$ (40 cm^3, 0.96 mmol). As the white suspension vanished, a dark red-brown residue was deposited. After 0.5 h, further stirring, the supernatant was filtered off and the residue was extracted with hot (75 °C) toluene. The red-brown filtrate was cooled (−30 °C), yielding fine brown-maroon plates of $\mathrm{Cr(2\text{-}ad)_4}$. These were recrystallised once more from toluene (0.18 g, 32%).

Bis(1-*adamantyl*)*magnesium*.—To a solution of $\mathrm{Mg(1\text{-}ad)Br}$ [3a] (105 cm^3 of 1.16 mol dm^{-3}, 16.8 mmol) in diethyl ether at ambient temperature was slowly added 1,4-dioxan (2.2 cm^3). The suspension was stirred for 6 h and the solid compacted by centrifugation. The liquors were filtered off and the solvents distilled out *in vacuo*. The product was heated at 100 °C (10^{-2} Torr) for 6 h to remove dioxan and adamantylic by-products. (Yield: 2.34 g, 95% based on MgRBr.) The complex could be recrystallised from diethyl ether, giving white needles of the etherate $\mathrm{MgR_2{\cdot}2OEt_2}$. The compound $\mathrm{Mg(1\text{-}ad)_2}$ is only slightly soluble in hydrocarbons, but unlike the organolithium analogue,[3b] it does not decompose in diethyl ether.

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