COMMUNICATIONS

solution. As a result, a $Ni_{32}C_6^6$ molecular ion, which is identical to the $Cr_{32}C_6$ building unit of the $Cr_{23}C_6$ carbide, ^[7, 13] has now been stabilized in a shell of 36 carbonyl ligands. The isolation and characterization of **3** a₁₅₀ substantiates the linear combination of Guassian type orbitals-local density functional (LCG-TO-LDF) study previously carried out on a $[Ni_{32}C_6(CO)_{36}]^n$ model compound.^[16]

The space-filling model in Figure 2 illustrates an interesting feature of **3**: the structure shows eight distorted hexagonal cupshaped hollows formed by consecutive concentric rings of oxy-



Fig. 2. Space-filling model of 3 illustrating one of the eight cup-shaped hollows.

gen, carbon, and nickel atoms, and ending with an unique nickel atom belonging to the inner cube. We are currently investigating the possibility of placing sterically less demanding molecules in these cup-shaped hollows, as well as the potential use of 3 as a molecular precursor for the preparation of the unknown $Ni_{23}C_6$ alloy.

Experimental Procedure

A solution of $[PPh_3Me]_6-2$ (350 mg, 0.067 mmol) in acetonitrile (20 mL) was stirred under a CO atmosphere for 15 min and then evaporated under vacuum to dryness. The residue was dissolved in acetonitrile (20 mL) and stirred under a CO atmosphere for 10 min and then dried under vacuum. The resulting dark brown residue was extracted with acetonitrile (20 mL) and filtered. Precipitation by layering the extract with diisopropyl ether (40 mL) gave black crystals of $[PPh_3Me]_6[Ni_{32} C_6(CO)_{36}]-4$ MeCN (210 mg, 0.043 mmol). The salt is soluble in acetone, acetoni trile, and dimethyl sulfoxide, insoluble in THF, alcohols, and nonpolar solvents (v_{co} in MeCN at 1889 cm⁻¹). Elemental analysis for $[PPh_3Me]_6[Ni_{32}C_6(CO)_{36}]-$ 4 MeCN: calcd C 41.08, H 2.50, N 1.17; found C 40.86, H 2.41, N 1.14.

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- [2] I. Dance, K. Fischer, Prog. Inorg. Chem. 1994, 41, 637.
- [3] L. C. Roof, J. W. Kolis, Chem. Rev. 1993, 93, 1037.
- [4] J. M. van Ruitenbeek, D. A. van Leeuwen, L. J. de Jongh in *Physics and Chem-istry of Metal Cluster Compounds, Vol. 18* (Ed.: L. J. de Jongh), Kluwer, Dord-recht, **1994**, p. 277.
- [5] N. Rösch, G. Pacchioni in Clusters and Colloids: From Theory to Applications, (Ed.: G. Schmid), VCH, Weinheim, 1994, p. 5.
- [6] A. Ceriotti, A. Fait, G. Longoni, G. Piro, F. Demartin, M. Manassero, N. Masciocchi, M. Sansoni, J. Am. Chem. Soc. 1986, 108, 8091.
- [7] A. L. Bowman, G. P. Arnold, E. K. Storms, N. G. Neresov, Acta Crystallogr. Sect. B, 1972, 28, 3102.
- [8] A. Ceriotti, G. Longoni, M. Manassero, N. Masciocchi, L. Resconi, M. Sansoni, J. Chem. Soc. Chem. Commun. 1985, 181.

- [9] A. Ceriotti, A. Fait, G. Longoni, G. Piro, L. Resconi, F. Demartin, M. Manassero, N. Masciocchi, M. Sansoni, J. Am. Chem. Soc. 1986, 108, 5370.
- [10] A. Ceriotti, G. Longoni, M. Manassero, N. Masciocchi, G. Piro, L. Resconi, M. Sansoni, J. Chem. Soc. Chem. Commun. 1985, 1402.
- [11] Crystal data for [PPh₃Me]₆ [Ni₃₂C₆(CO)₃₆] 4 MeCN: triclinic, space group PI (No. 2), a = 15.974(3), b = 17.474(3), c = 18.200(4) Å, $\alpha = 61.37(2)$, $\beta = 12.200(4)$ Å, $\alpha = 61.37(2)$, $\beta = 12.200(4)$ Å, $\alpha = 61.37(2)$, $\beta = 12.200(4)$ Å, $\beta = 12.200(4)$ Å, $\alpha = 61.37(2)$, $\beta = 12.200(4)$ Å, $\beta = 12.200(4)$ Å, $\beta = 12.200(4)$ Å, $\alpha = 61.37(2)$, $\beta = 12.200(4)$ Å, $\beta = 12.200(4)$ Å, $\alpha = 61.37(2)$, $\beta = 12.200(4)$ Å, $\alpha = 12.200(4)$ Å 69.31(2), $\gamma = 72.35(2)^{\circ}$, V = 4115(1) Å³, Z = 1, $\rho_{calcd} = 1.93$ g cm⁻³, Mo_{Ku} radiation ($\lambda = 0.71073$ Å), $\mu(Mo_{Ka}) = 37.1$ cm⁻¹, T = 298 K. 14585 reflections with $3^{\circ} < \theta < 25^{\circ}$ were measured on a CAD4 diffractometer at room temperature using a crystal with approximate dimensions $0.20 \times 0.15 \times 0.35$ mm. Data were corrected for Lorentz-polarization and absorption effects (empirical absorption, transmission factors in the range 0.56-1.00). The structure was solved by direct methods (SIR 89) and refined by using 10639 independent reflections having $I > 3\sigma(I)$. Anisotropic displacement parameters were assigned to all non-hydrogen atoms. The final R value was 0.033 ($R_w = 0.043$). Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-179-79. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: Int. code +(1223) 336-033; e-mail: teched@chemcrys.cam.ac.uk).
- [12] G. Ertl in Metal Clusters in Catalysis, Vol. 29 (Eds.: B. C. Gates, L. Guczi, H. Knözinger), Elsevier, Amsterdam, 1986, p. 577.
- [13] The Cr₂₃C₆ alloy has a *Fm3m* structure [7], which conforms to the No. 24 of Andreini's space-filling combination of polyhedra [14,15]. It derives from a three-dimensional sequence of fused Cr₃₂C₆ truncated octahedra and Cr₁₃-centered cuboctahedra; this architecture generates truncated tetrahedra that are centered by further chromium atoms.
- [14] A. Andreini, Mem. Soc. Ital. Sci. 1907, 14, 75.
- [15] A. F. Wells, Three-Dimensional Nets and Polyhedra, Wiley, New York, 1977, p. 145.
- [16] N. Rösch, L. Ackermann, G. Pacchioni, J. Am. Chem. Soc. 1992, 114, 3549.

The Aluminocenium Cation $[Al(C_5H_5)_2]^+$: A Highly Effective Initiator for the Cationic Polymerization of Isobutene**

Manfred Bochmann* and David M. Dawson

Dedicated to Professor Sir Geoffrey Wilkinson on the occasion of his 75th birthday

The role of aluminum reagents as Lewis acids and as activators for olefin polymerization catalysts is well documented.^[1] Very little is known, however, about the chemistry of cationic organoaluminum compounds $[AlR_2]^+$ for which very high Lewis acidity can be expected. Some donor-stablized cationic complexes such as $[AlMe_2(crown)]^+$, $[(EtAl)_2(diazacrown)]^{2+}$, and $[Al\{C(SiMe_3)_2py\}_2]^+$ have been structurally characterized,^[2, 3] and recently Schnöckel et al. reported the formation of the decamethylaluminocenium cation $[AlCp_2]^+$ by the disproportionation of $[AlCp^*]_4$ in the presence of $AlCl_3$ (Cp* = C_5Me_5).^{[41} The reactivity of such cationic organoaluminum complexes has to our knowledge not been explored. We report here the synthesis of the unsubstituted aluminocenium cation, $[AlCp_2]^+$, (Cp = C_5H_5) and its reactivity as an initiator for cationic polymerizations.

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G. Longoni, M. C. Iapalucci in Clusters and Colloids: From Theory to Applications (Ed.: G. Schmid), VCH, Weinheim, 1994, p. 91.

The reaction of $[AlCp_2Me]$ (1)^[5] with $B(C_6F_5)_3$ (2) in dichloromethane at low temperature, followed by evaporation of the solvent affords the white microcrystalline solid 3 [Eq. (a)].^[6] Compound 3 is sparingly soluble in warm benzene



or toluene but dissolves rapidly in cold dichloromethane. Over the temperature range from -80 to -20 °C, solutions of **3** in CD₂Cl₂ show two singlets in the ¹H NMR spectrum at $\delta = 7.05$ and 0.55, consistent with the formation of the solvated ion pair [AlCp₂]⁺[MeB(C₆F₅)₃]⁻. These solutions decompose rapidly on warming them to 20 °C. The ²⁷Al NMR spectrum recorded at -60 °C for the reaction of **1** with **2** shows that the broad signal for **1** at $\delta = 72.7$ (half-width ca. 250 Hz) is replaced by a new sharp peak at $\delta = -126.4$ (half-width 30 Hz). This value is in excellent agreement with the calculated chemical shift for the [Al(η^{5} -Cp)₂]⁺ ion ($\delta = -130.0$).^[4]

1:1 mixtures of 1 and 2 in $[D_8]$ toluene at 20 °C show very similar ¹H and ²⁷Al NMR spectra. The limited solubility of the reaction product in toluene leads to the formation of two phases on cooling. Although the formation of the methyl-bridged isomer $[Cp_2Al(\mu-Me)B(C_6F_5)_3]$ might reasonably be expected in less polar solvents, conclusive evidence for this was not found.

Even in the solid state 3 is highly air- and moisture-sensitive. Unfortunately crystals suitable for X-ray diffraction could not be obtained. Although 1 has been shown to contain η^2 -coordinated Cp rings in the crystal and is highly fluxional in solution, the [AlCp₂]⁺ ion most likely possesses a metallocene-type structure with η^{5} -bound Cp ligands. This assumption is supported by the structure of $[Al(\eta^5 - Cp^*)_2]^+$, the close agreement of the observed ²⁷Al chemical shift with the one calculated assuming a $D_{\rm 5d}$ symmetry. the narrow half-width of the ²⁷Al signal, which is typical for a highly symmetric ligand environment for Al, as well as the sandwich structures of the isoelectronic magnesiocene [MgCp₂] and related Group 2 cyclopentadienyl complexes.^[7] An increase in hapticity from η^1 to η^5 on forming a more Lewis acidic cationic metal center from a neutral cyclopentadienyl complex is also a common feature of boron cyclopentadienyl complexes.^[8]

Starting point for the synthesis of $[AlCp_2]^+$ was the search for highly Lewis acidic compounds as initiators for carbocationic polymerizations. Compound 3 is indeed a highly active initiator for the polymerization of isobutene and isobutene – isoprene copolymerizations [Eq. (b)]. Such copolymerizations to butyl rub-



ber are carried out on an industrial scale by using a heterogeneous initiator based on AlCl₃ in chloromethane at between -95 and -100 ⁵C.^[9, 10] The need to recycle large amounts of chlorinated solvents and the high energy requirements of such a low-temperature process make cleaner, less energy intensive al-

ternatives that can be operated at higher temperatures highly desirable.

The activity of 3 as an initiator for the polymerization of isobutene has been studied over a temperature range of -78 °C to -25 °C. The reactions proceed in dichloromethane as well as in saturated hydrocarbons. Neither 1 nor 2 on their own was found to polymerize isobutene.^[11] Whereas an excess of 2 over 1 has no effect on polymer yield or molecular weight, an excess of 1 over 2 retards the polymerization. The results for isobutene homopolymerizations are given in Table 1. As expected for carbocationic polymerizations, the polymer molecular weights increase with decreasing temperature, from $M_w \approx 3 \times 10^5$ at -30 °C to 1.8×10^6 at -70 °C, with narrow polydispersities.^[12]

Table 1. Isobutene homopolymerizations initiated with 3 [a].

Entry	l [μmol]	2 [μmol]	T [C]	t [min]	Yield [g]	$\frac{M_{\rm w}}{\rm x10^{-3}}$	$M_{ m w}/M_{ m n}$
1 [b]	40	40	- 78	10	0.63	731	3.0
2 [c]	38	38	- 78	10	0.28	1340	3.0
3	50	50	-70	10	0.30	1800	2.8
4	100	50	-70	10	0.02	820	3.4
5	50	50	- 50	10	0.18	618	2.0
6	50	50	- 30	10	0.08	318	1.8
7	50	100	- 30	10	0.03	337	1.8
8	50	50	-25	10	0.05	289	1.6

[a] For reaction conditions see Experimental Procedure. Entries 3 -8: Polymerizations were carried out in the presence of 1.5 mL dichloromethane. [b] Solvent: toluene (1.5 mL). [c] Solvent: methylcyclohexane (1.5 mL).

Compound 3 also initiates the copolymerization of isobutene with 2-5 vol% of isoprene, at typical reaction temperatures of -78 to -50 °C. For example, the reaction with 5% isoprene at -70 °C gave a polymer with $M_w = 7.8 \times 10^5$ and $M_w/M_n = 3.3$. The polymer contained about 2.7% isoprene units with a 1.4trans structure; there was no evidence for 1.4-*cis* or 1.2-incorporation within NMR detection limits.^[13] Similar reactions with 2 vol% isoprene at -50 °C gave copolymers with $M_w \approx 2 \times 10^5$.

It is likely that the relatively high molecular weights obtained in these reactions are not least due to the weakly basic nature of the counteranion used in this system. Isobutene homo- and copolymerizations are usually carried out with a mixture of a Lewis acidic metal halide MX, and an alkyl halide RX capable of generating a carbocation, resulting in the formation of $R^{+}[MX_{n+1}]^{-}$. Self-ionization of the Lewis acid to $[MX_{n-1}]^{+}$ $[MX_{n+1}]^{-}$ has also been suggested, although there is so far no direct evidence for species such as [AlX₂]⁺ in polymerization systems.^[14] Complex halide anions $[MX_{n+1}]^-$ possess rather limited stability and are prone to loss of X⁻ ions, which may lead to halide incorporation into the polymer and may assist deprotonation and chain transfer. In the present case we make use of the stability and very low basicity of perfluorophenylborates to generate a well-defined polymerization initiator system free of halide anions.[15, 16]

Experimental Procedure

All reactions were carried out under strictly dry and anaerobic conditions. NMR spectra were measured on JEOL EX270 and Bruker DPX300 spectrometers (reference: tetramethylsilane: ¹H and ¹³C; $[Al(H_2O)_6]^{3+;}$ ²⁷Al). Isobutene was dried over El₂AlOC₆H_{1,1} and recondensed; isoprene was dried over calcium hydride and distilled from sodium prior to use.

3: To a solution of 1 (400 mg, 2.3 mmol) in dichloromethane (10 mL) at -78 C was added 2 (1.2 g, 2.3 mmol). The mixture was stirred for 15 min, and the solution allowed to warm to 0 °C whilst the solvent was removed in vacuo. The off-white solid residue was washed with light petroleum and dried to give 3 (1.6 g, 2.3 mmol, 99%). Elemental analysis: Found: C 50.13, H 1.90, F 41.2%; calc.: C 50.87, H 1.90,

F 41.6%; ¹H NMR (CD₂Cl₂, -60° C): $\delta = 0.55$ (s, 3 H, Me-B), 7.05 (s, 10 H, Cp); ¹³C NMR (CD₂Cl₂, -20° C): $\delta = 10.5$ (s, br, Me-B), 114.5 (s, Cp); ²⁷Al NMR (CD₂Cl₂, -20° C): $\delta = -126.35$; ([D₈]toluene, 20° C): $\delta = -128.3$ (half-width ca. 30 Hz).

(Co-)Polymerizations were carried out in an all-glass reactor, which was flame-dried in vacuo. Isobutene (10 mL) was condensed into the reaction vessel and magnetically stirred at 1000 rpm to allow it to equilibrate at the appropriate temperature. This was followed by injection of 2 (50 µmol) in 1 mL of solvent (cf. Table 1). The mixture was stirred for 1 min before 1 (50 µmol) in 0.5 mL solvent were injected. Polymerization took place instantaneously. The polymerization was terminated by injecting 0.5 mL methanol, and the polymer precipitated by the addition of further methanol. The product was filtered and dried in an oven at 60 °C. For copolymerizations the condensation of isobutene was followed by an injection of 2-5 vol% isoprene.

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- [1] J. J. Eisch in Comprehensive Organometallic Chemistry, Vol 1 (Eds.: G. Wilkinson, F. G. A. Stone, E. W. Abel), Pergamon, 1982, p. 555ff; Comprehensive Organometallic Chemistry II, Vol. 1, Pergamon, 1995, p. 431ff.
- [2] S. G. Bott, A. Alvanipour, S. D. Morley, D. A. Atwood, C. Mitchell Means, A. W. Coleman, J. L. Atwood, *Angew. Chem.* **1987**, *99*, 476; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 485; H. G. Richey, G. L. Bergstresser, *Organometallics* **1988**, *7*, 1459; M. F. Self, W. T. Pennington, J. A. Laske, G. H. Robinson, *ibid* **1991**, *10*, 36.
- [3] L. M. Engelhardt, U. Kynast, C. L. Raston, A. H. White, Angew. Chem. 1987, 99, 702; Angew. Chem. Int. Ed. Engl. 1987, 26, 681.
- [4] C. Dohmeier, H. Schnöckel, C. Robl, U. Schneider, R. Ahlrichs, Angew. Chem. 1993, 105, 1714; Angew. Chem. Int. Ed. Engl. 1993, 32, 1655.
- [5] J. Stadelhofer, J. Weidlein, A. Haaland, J. Organomet. Chem. 1975, 84, C1; J. D. Fisher, M. Y. Mei, R. Willet, P. J. Shapiro, Organometallics 1994, 13, 3324. In this reference a ¹³C NMR signal at $\delta = 14.05$ is quoted for Al-CH₃. In our experience pure, petroleum ether free AlCp₂Me does not exhibit such a resonance.
- [6] The reaction of t with [CPh₃][B(C₆F₅)₄] proceeds similarly but is less clean and appears to involve abstraction of Cp as well as methyl anions by [CPh₃]⁺.
- [7] W. Bünder, E. Weiss, J. Organomet. Chem. 1975, 92, 1; T. P. Hanusa, Polyhedron 1990, 9, 1345.
- [8] P. Jutzi, A. Seufert, J. Organomet. Chem. 1978, 161, C5; P. Jutzi, A. Seufert, W. Buchner, Chem. Ber. 1979, 112, 2488.
- [9] I. M. Campbell, Introduction to Synthetic Polymers, Oxford University Press, Oxford 1994, p. 130.
- [10] J. P. Kennedy, B. Iván, Designed Polymers by Carbocationic Macromolecular Engineering, Hanser, Munich 1991.
- [11] In the presence of moisture 2 gives the acidic hydrate $B(C_6F_s)_3 \cdot H_2O$, which results in H⁺-initiated formation of polyisobutene of variable molecular weight. Traces of moisture lead to very small amounts of high molecular weight polyisobutene ($M_w = ca. 2-3 \times 10^6$), typical for very low initiator concentrations.
- [12] Very similar polymerization results were obtained with the system [Al-Cp(R)Cl]/2 (R = Me, Et). Monitoring the reaction between [AlCpMeCl] and 2 in CD₂Cl₂ at -73 °C shows the formation of [AlCp₂]⁺ as the only identifiable product, evidently formed by Cp ligand exchange.
- [13] J. L. White, T. D. Shaffer, C. J. Ruff, J. P. Cross, Macromolecules 1995, 28, 3290.
- [14] L. Balogh, Z. Fodor, T. Kelen, R. Faust, Macromolecules 1994, 27, 4648. Dialkylaluminum cations have been generated in the gas phase: R. Srinivas, D. Sülzle, H. Schwarz, J. Am. Chem. Soc. 1990, 112, 8334.
- [15] M. Bochmann, Angew. Chem. 1992, 104, 1206; Angew. Chem. Int. Ed. Engl. 1992, 31, 1181. For the use of metal alkyl/B(C₆F₈)₃ systems in Ziegler-type olefin polymerizations see for example X. Yang, C. L. Stern, T. J. Marks, J. Am. Chem. Soc. 1991, 113, 3623; ibid. 1994, 116, 10015; M. Bochmann, J. Chem. Soc., Dalton Trans. 1996, 255, and references therein.
- [16] Since this work was started, the cationic polymerization of isobutene with a [Cp*TiMe₃]/B(C₆F₅)₃ initiator system has been reported: F. Barsan, M. C. Baird, J. Chem. Soc. Chem. Commun. 1995, 1065. The polyisobutene molecular weights reported for this system, which range from 3 × 10⁴ (- 20 °C) to 2 × 10⁵ (-78 °C), are significantly lower than those obtained here with [AlCp₂]⁺.

From $1\sigma^4, 2\sigma^2$ to $1\sigma^4, 2\sigma^n$ -Diphosphetes (n = 3-6): The Surprising Persistence of the P-P bond**

Muriel Sanchez, Régis Réau, Françoise Dahan, Manfred Regitz, and Guy Bertrand*

Dedicated to Professor Miha Tišler on the occasion of his 70th birthday

The phosphanylidene- σ^4 -phosphorane **A** was reported by Burg and Mahler in 1961.^[1] It was the first example of a two-coordinate phosphorus atom in a neutral molecule, but more importantly, this compound opened the way to a variety of new types of P-P bonding beyond the classical ones (**B**-**D**) accepted



at that time.^[2] Among other resonance forms, **A** can be regarded as a phosphane complex of a phosphinidene (phosphanediyl) unit.^[3] Since phosphinidene units feature a phosphorus atom with the lowest possible coordination number, it is surprising that they have not been used more frequently to prepare phosphorus derivatives with much higher coordination states.^[4] Very recently, we reported the synthesis of the $1\sigma^4$, $2\sigma^2$ -diphosphete 1,^[5] a cyclic phosphanylidene- σ^4 -phosphorane, and herein we report the conversion of the low-coordinate phosphorus centers of 1 into a succession of higher coordinate phosphorus centers; the P-P interaction and the cyclic structure is retained throughout this series.

One of the rare examples of reactivity known for derivatives of type **A** is methylation.^[3, 6] Thus, heterocycle **1** was treated with methyl triflate, which led to the cationic $1\sigma^4, 2\sigma^3$ -diphosphete **2** in 95% yield (Scheme 1); selective spectroscopic data are given in Table 1. The cyclic structure is supported by the high-field shift of the ³¹P NMR resonance of the PMe unit $(\delta = + 54.9)$, the small ²J(PNCH) coupling constants (5.2 and 4.8 Hz) typical of a diisopropylamino-substituted σ^4 -phosphorus atom,^[7] and by the multiplicity of the ¹H ($\delta = 1.84$, dd, J(P,H) = 19.1 and 4.9 Hz) and ¹³C NMR ($\delta = 11.26$, dd, J(P,C) = 42.0 and 8.5 Hz) signals of the P-methyl group. Note the relatively small value of J(P,P) (107.4 Hz), which results from superimposition of the ¹J and ³J coupling constants.

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^[**] This work was supported by the Centre National de Recherche Scientifique (CNRS), the Fonds der Chemischen Industrie (Graduiertenkolleg Phosphor), and the Deutsche Forschungsgemeinschaft. Editorial note: According to IUPAC recommendations, when ring atoms display a connectivity that differs from their standard bonding number, the actual bonding number is expressed as an arabic superscript to the Greek letter lambda following immediately after the appropriate locant. In this communication, however, contrary to this recommendation the Greek letter sigma has been applied to highlight the structural connection between the compounds 1-6. The superscript, here gives the number of o bonds starting from the ring phosphorus atoms.