

$1^+$  as a key intermediate. Preference for electron transfer over hydride transfer in the reaction of **1** with the trityl cation is revealed by competitive atom-transfer trapping of  $1^+$  with  $[\text{BrMn}(\text{CO})_5]$ . These experiments establish a two-step eH mechanism rather than a concerted hydride transfer for the reaction of **1** with the trityl cation. Under the conditions of reduction with  $\text{H}_2$  eH hydride transfer is interrupted, which results instead in the accumulation of Gomberg's dimer derived from one-electron reduction of the trityl cation.

Due to the role of **1** in converting  $\text{H}_2$ , a two-electron reducing agent, into a reductant for two one-electron steps, we refer to it as a "redox-switch" catalyst. Further studies of this unprecedented transfer of electrons from the H–H bond of hydrogen to C–C bonds by one-electron reduction of carbenium ions are in progress.

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- [1] Halpern and co-workers reported studies of odd-electron reductions with  $\text{H}_2$  of inorganic oxidants such as the  $\text{Cr}_2\text{O}_7^-$ ,  $\text{MnO}_4^-$ , and  $[\text{Fe}(\text{phen})_3]^{3+}$  [2]. Little elaboration on this seminal work has been reported in the extensive development of hydrogenation catalysis during the intervening three and a half decades.
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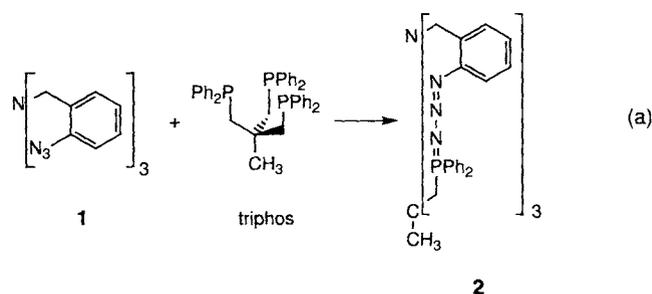
## New Cage Compounds: Preparation and Characterization of Chiral $\text{C}_3$ -Symmetric Macrobicyclic Tris(phosphazides)\*\*

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The formation of medium and large ring systems is a permanent challenge for synthetic chemists, as special skills are usually required for the cyclization, although self-assembly and pre-organization of the reactants can minimize undesirable oligomerizations. Phosphorus-containing macrocycles are now well-documented, but those with intracyclic P–N units are scarce.<sup>[1]</sup> Macrocyclization reactions involving P–N bond formation have been rarely explored.<sup>[1c]</sup>

$\text{CH}_3\text{C}(\text{CH}_2\text{PPh}_2)_3$  (triphos), the most widely investigated tripodal polyphosphane, is an excellent ligand of increasing significance in coordination chemistry.<sup>[2]</sup> However, little is known about the chemistry of triphos other than its extraordinary coordinating ability, and no reactions with azides have been reported.

Tris(azide) **1** was prepared by standard chemistry starting from bis(*o*-azidobenzyl)amine<sup>[3]</sup> and *o*-azidobenzyl chloride.<sup>[4]</sup> The reaction of equimolar amounts of **1** and triphos at room temperature provided microcrystalline **2** in 66% yield [Eq. (a)].



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In the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **2** ( $\text{CDCl}_3$ ) the singlet at  $\delta = 1.34$  is in the range<sup>[5]</sup> typical for phosphazides<sup>[6]</sup> 25–30 ppm downfield relative to the resonance of the phosphane counterpart (triphos  $\delta = -27.3$ ),<sup>[7]</sup> which reflects the high symmetry of **2** (probably  $C_3$ ). The same holds for the  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra, where only one set of signals is present (Table 1). The

Table 1. Selected physical data of tris(phosphazides) **2** and **4** [a].

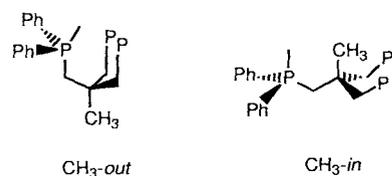
**2**: M.p. 254–256 °C; IR (Nujol):  $\bar{\nu} = 1146$  (vs), 1112 (vs) (PN), 696 (vs)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta = -0.12$  (br. s, 3H,  $\text{CH}_3$ ), 3.66 (d,  $J = 12.9$  Hz, 3H,  $\text{NCH}_2\text{H}_B$ ), 3.88 (d,  $J = 12.9$  Hz, 3H,  $\text{NCH}_2\text{H}_B$ ), 3.92 (m, 3H,  $\text{PCH}_2\text{H}_B$ ), 4.24 (pseudo t,  $J = 14.1$  Hz, 3H,  $\text{PCH}_2\text{H}_B$ ), 6.90–7.40 (m, 30H), 7.59 (d,  $J = 7.5$  Hz, 3H), 7.90 (d,  $J = 8.1$  Hz, 3H), 8.05–8.12 (m, 6H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta = 26.36$  (br. s,  $\text{CH}_3$ ), 36.51 (m,  $\text{PCH}_2$ ), 40.64 (q,  $^2J(\text{C,P}) = 4.7$  Hz,  $\text{CH}_2\text{C}$ ), 55.61 (s,  $\text{NCH}_2$ ), 116.71 (s, CH arom.), 126.27 (s, CH arom.), 127.30 (s, CH arom.), 128.35 (d,  $^1J(\text{C,P}) = 104.5$  Hz, *ipso*-C, PPh), 128.62 (d,  $^1J(\text{C,P}) = 83.2$  Hz, *ipso*-C, PPh), 128.64 (d,  $^3J(\text{C,P}) = 11.2$  Hz, *m*-C, PPh), 128.74 (d,  $^3J(\text{C,P}) = 11.8$  Hz, *m*-C, PPh), 130.13 (d,  $^2J(\text{C,P}) = 9.0$  Hz, *o*-C, PPh), 130.39 (s, CH arom.), 131.30 (d,  $^4J(\text{C,P}) = 2.9$  Hz, *p*-C, PPh), 131.86 (d,  $^4J(\text{C,P}) = 2.3$  Hz, *p*-C, PPh), 132.45 (d,  $^2J(\text{C,P}) = 7.8$  Hz, *o*-C, PPh), 132.88 (s, C- $\text{CH}_2\text{N}$ ), 147.78 (s,  $\text{CN}_3$ );  $^{31}\text{P}\{^1\text{H}\}$  NMR (121.5 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta = 1.34$  (s); FAB<sup>+</sup> MS:  $m/z$  (%): 1036 ( $M^+ + \text{H}$  calcd for  $\text{C}_{62}\text{H}_{58}\text{N}_{10}\text{P}_3$  1036.1)

**4**: M.p. 270–272 °C; IR (Nujol):  $\bar{\nu} = 1157$  (vs), 1125 (vs) (PN), 692 (vs)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta = -0.03$  (br. s, 3H,  $\text{CH}_3$ ), 3.85 (pseudo t,  $J = 14.0$  Hz, 3H,  $\text{PCH}_2\text{H}_B$ ), 4.10 (m, 3H,  $\text{PCH}_2\text{H}_B$ ), 4.18 (d,  $J = 13.1$  Hz, 3H,  $\text{NCH}_2\text{H}_B$ ), 4.96 (d,  $J = 13.1$  Hz, 3H,  $\text{NCH}_2\text{H}_B$ ), 6.90–7.43 (m, 30H), 8.05 (d,  $J = 8.4$  Hz, 3H), 8.06–8.15 (m, 6H), 9.00 (d,  $J = 7.8$  Hz, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta = 25.66$  (br. s,  $\text{CH}_3$ ), 37.10 (m,  $\text{PCH}_2$ ), 40.33 (q,  $^2J(\text{C,P}) = 3.5$  Hz,  $\text{CH}_2\text{C}$ ), 66.74 (s,  $\text{NCH}_2$ ), 116.05 (s, CH arom.), 126.22 (s, CH arom.), 126.44 (s, C- $\text{CH}_2\text{N}$ ), 127.67 (d,  $^1J(\text{C,P}) = 81.6$  Hz, *ipso*-C, PPh), 127.70 (d,  $^1J(\text{C,P}) = 109.3$  Hz, *ipso*-C, PPh), 128.89 (d,  $^3J(\text{C,P}) = 11.1$  Hz, *m*-C, PPh), 129.01 (s, CH arom.), 129.03 (d,  $^3J(\text{C,P}) = 10.6$  Hz, *m*-C, PPh), 129.98 (d,  $^2J(\text{C,P}) = 9.5$  Hz, *o*-C, PPh), 131.77 (d,  $^4J(\text{C,P}) = 3.0$  Hz, *p*-C, PPh), 132.15 (d,  $^2J(\text{C,P}) = 7.6$  Hz, *o*-C, PPh), 132.21 (d,  $^4J(\text{C,P}) = 2.3$  Hz, *p*-C, PPh), 132.48 (s, CH arom.), 147.87 (s,  $\text{CN}_3$ );  $^{31}\text{P}\{^1\text{H}\}$  NMR (121.5 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta = -1.41$  (s); FAB<sup>+</sup> MS:  $m/z$  (%): 1052 ( $M^+ + \text{H}$  calcd for  $\text{C}_{62}\text{H}_{58}\text{N}_{10}\text{OP}_3$  1052.1)

[a] The new compounds gave satisfactory C,H,N elemental analyses; H,H-COSY experiments and high-resolution  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were used for accurate assignments.

diastereotopicity of the methylene protons in the  $\text{CH}_2\text{-P}$  and  $\text{CH}_2\text{-N}$  groups speaks for intrinsic chirality and therefore for the helical or propellerlike shape of the molecule. Particularly noteworthy is the chemical shift of the  $\text{CH}_3$  protons ( $\delta = -0.12$ , broad singlet), which is 1.07 ppm upfield relative to the analogous signal in the phosphane<sup>[7]</sup> and far away from the signals of most of the known triphos transition metal complexes, which lie in the range  $\delta = 1.12\text{--}2.09$ .<sup>[8]</sup> Also, the shifts of the  $\text{CH}_2\text{-P}$  protons ( $\delta = 3.92$  and 4.24) are notably different from those in the phosphane ( $\delta = 2.48$ )<sup>[7]</sup> and its complexes ( $\delta = 2.06\text{--}2.78$ ).<sup>[8]</sup> These data raised the question of the conformation of the triphos fragment in compound **2**. Does it have the  $\text{CH}_3\text{-out}$  conformation found in all the known triphos complexes in which the ligand is coordinated in an  $\eta^3$  fashion, the previously not reported  $\text{CH}_3\text{-in}$  conformation (Scheme 1), or some other conformation imposed by the particular topology of the molecule?<sup>[9]</sup>

In this context, we observed that, like the methyl protons, the  $\text{CH}_3$  carbon atom of **2** is also shielded (broad singlet at  $\delta = 26.36$ ;  $\delta = 29.5$  and 36–40 in the phosphane and its complexes, respectively)<sup>[7, 8]</sup>. In the  $^{13}\text{C}$  NMR spectrum the two diastereotopic phenyl rings linked to each phosphorus atom appear to be



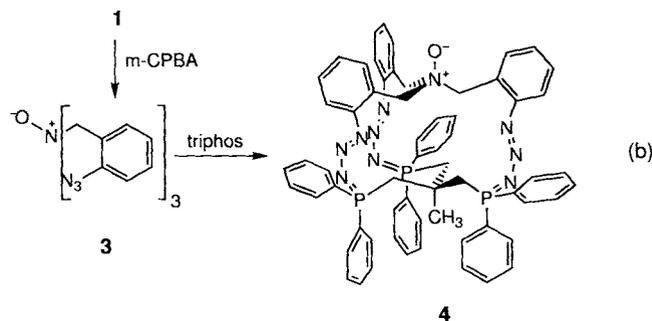
Scheme 1. The two known conformations of triphos depicting the position of the  $\text{CH}_3$  group

magnetically inequivalent with notable differences in the coupling constants  $^1J(\text{C,P})$  for the two *ipso* carbon atoms (83.2 and 104.5 Hz). This unusual fact probably reflects a not exactly tetrahedral environment at the phosphorus atoms.

Since the NMR spectra did not change when the sample was cooled to 203 K, significant dynamic processes for compound **2** at room temperature can be excluded. Because of the chemical instability of this tris(phosphazide) its apparent conformational rigidity could not be evaluated by high-temperature NMR experiments. In  $\text{CDCl}_3$  **2** decomposed totally in 24 h at 298 K and in 2 h at 323 K, giving an intractable mixture.

All this data indicate unequivocally that compound **2** is a tris(phosphazide). Phosphazides typically lose dinitrogen at ambient or even lower temperature to produce  $\lambda^5$ -phosphazenes,<sup>[10]</sup> although some phosphazides have been isolated.<sup>[10b]</sup> The X-ray structural data of six phosphazides<sup>[11]</sup> showed as common features the essentially zwitterionic character of the  $\text{PN}_3$  framework ( $\text{P}^+ - \text{N} = \text{N} - \text{N}^-$ ) and the *E* configuration of the central  $\text{N} = \text{N}$  bond. Attempts to build reasonable molecular models of tris(phosphazide) **2** with (*E*)- $\text{PN}_3$  frameworks, with four possible combinations of the conformations around the bridgehead N and quaternary  $\text{sp}^3$  carbon atoms (N lone pair *in* or *out*,  $\text{CH}_3$  *in* or *out*), gave highly strained structures. Unfortunately, we were unable to obtain a crystalline sample of **2** suitable for X-ray structure determination.

We reasoned that the lability of **2** in solution could result from the initial dissociation of one  $\text{PN}_3$  arm into phosphane and azide,<sup>[12]</sup> and that this dissociation could be facilitated by the inversion of the configuration at the bridgehead N atom. To suppress this inversion we decided to prepare similar tris(phosphazides) in which that N atom is quaternized. Derivatization of **2** by protonation with acids or methylation with methyl iodide, triflate, or tetrafluoroborate gave only intractable complex mixtures. Although tris(azide) **1** was easily protonated and methylated, the resulting ammonium salts did not react efficiently with triphos. Finally reaction of the tertiary amine N-oxide **3**, easily prepared from **1** by the action of *m*CPBA,<sup>[13]</sup> with triphos provided the macrobicyclic tris(phosphazide) **4** [Eq. (b)].



Compound **4** was stable in  $\text{CDCl}_3$  solution for several days at room temperature without noticeable decomposition, and its analytical and spectroscopic data (Table 1) are in agreement with the proposed structure and very similar to those obtained for the tris(phosphazide) **2**. Suitable crystals of **4** now allowed an X-ray structure analysis.<sup>[14]</sup>

Two perspective views of the molecular structure of **4** are shown in Figure 1. The molecule is located on a threefold crystallographic axis passing through O1, N2, C15, and C16, and its propellerlike shape is clearly apparent when the molecule is viewed along this axis (Fig. 1b). Both O1 and C16 are located outside the cavity of the macrocycle. The  $\text{PN}_3$  fragment presents a *Z* configuration with respect to the central  $\text{N} = \text{N}$  bond

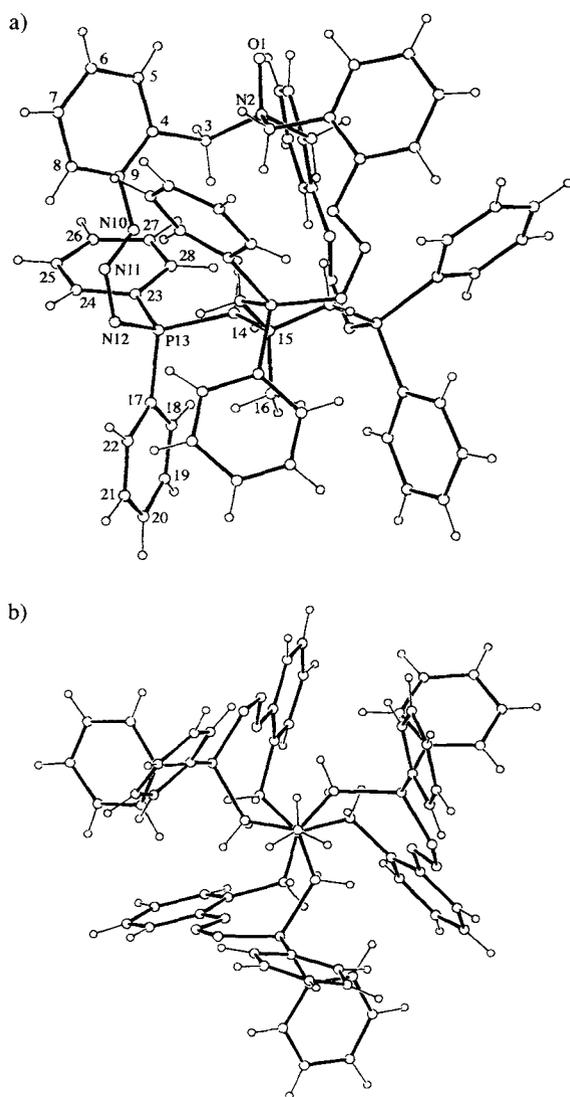


Figure 1. a) Molecular structure of **4**. Selected interatomic distances [Å] and angles [°]: O1–N2 1.344(15), N2–C3 1.519(11), N10–N11 1.257(12), N11–N12 1.340(11), N12–P13 1.640(8), P13–C14 1.810(11), P13–C17 1.791(10), P13–C23 1.799(8), N10–P13 2.714(7); O1–N2–C3 110.2(3), C9–N10–N11 114.7(7), N10–N11–N12 117.5(8), C14–P13–C17/C23/N12 108.5(5)/105.2(4)/119.9(4), C17–P13–C23/N12 106.1(4)/102.0(4), N10–P13–C14/C17/C23 88.5(3)/156.6(4)/83.8(3). b) A perspective view as projected along the threefold axis.

[N10–N11–N12–P13 =  $-7.5(11)^\circ$ ] in contrast to the *E* configuration observed in all the previously reported phosphazides.<sup>[11]</sup> There is extensive electronic delocalization in the P–N–N–N fragment and the distances compare fairly well with the average values of 1.630(1), 1.341(1), and 1.273(1) Å for the analogous *E*-phosphazides; the lengths of the N12–P13 and N11–N12 bonds are between those of single and double bonds [1.697(15), 1.582(19) Å for N–P bonds in phosphazenes, and 1.401(18), 1.245(9) Å for N–N bonds].<sup>[18]</sup> The environment of the phosphorus atom can be described as a tetrahedron distorted toward a trigonal bipyramid with N10 and C17 in axial positions (Fig. 1a). The P13...N10 distance is within the range of 2.592(7)–2.741(7) Å reported for related compounds that are intermediate to open-chain betaines and cyclic 1,3,2-diazaphosphetidines.<sup>[19]</sup> The hydrogen atoms of the C16 methyl group are 1.49 and 3.13 Å away from the C17–C22 and C23–C28 planes, respectively; the distances to the respective centroids are 3.51 and 6.19 Å.

Tris(phosphazide) **4** is notably more stable than **2** and is unchanged after several weeks in CDCl<sub>3</sub> solution at 298 K and also after mild heating (6 h, 334 K, CDCl<sub>3</sub>). High-temperature <sup>1</sup>H NMR experiments (CDCl<sub>3</sub>, from 298 to 330 K) showed no appreciable changes in the normal spectrum of **4**. Thus, in this range of temperatures the chiral, C<sub>3</sub>-symmetric structure is rigid and does not isomerize via labile conformations with C<sub>1</sub> symmetry.

### Experimental Section

General synthesis of **2** and **4**: Two solutions of the corresponding tris(azide) (10 mL, 1.5 mmol, 0.15 M in diethyl ether for **1**, and in dichloromethane for **3**) and triphos (10 mL, 1.5 mmol, 0.15 M in diethyl ether) were simultaneously added under nitrogen at room temperature over 30 min and with stirring, to a round-bottom flask containing 15 mL of diethyl ether. The resulting mixture was then stirred overnight, the precipitated pale yellow solid was filtered and dried under vacuum to give compounds **2** and **4** in 66 and 85% yield, respectively.

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**[(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Al–Fe(CO)<sub>4</sub>]<sup>–</sup>—  
Synthesis, Structure, and Bonding**

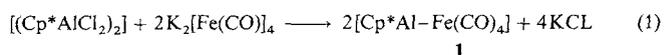
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The series of surprisingly stable subvalent halides and organometallic compounds of aluminum and gallium has extended over the last few years to include several interesting compounds that open up promising perspectives as starting materials for preparative purposes.<sup>[1]</sup> For instance the fascinating tetrahedral compound [(Cp\*Al)<sub>4</sub>]<sup>[2]</sup> its alkyl congeners (RE)<sub>4</sub> and R<sub>2</sub>E–ER<sub>2</sub> (R = (Me<sub>3</sub>Si)<sub>2</sub>CH, (Me<sub>3</sub>Si)<sub>3</sub>C; E = Al, Ga,

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In),<sup>[3]</sup> and [R<sub>2</sub>Al–AlR<sub>2</sub>]<sup>–</sup> (R = (Me<sub>3</sub>Si)<sub>2</sub>CH, 2,4,6-*i*Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)<sup>[3]</sup> are examples for Al–Al π bonding. Carbonylmetal complexes with donor-stabilized Al<sup>I</sup> and Ga<sup>I</sup> fragments such as (CO)<sub>5</sub>Cr–Ga(C<sub>2</sub>H<sub>5</sub>)L<sub>2</sub> (L<sub>2</sub> = tmeda) are also of interest, since they are suitable volatile precursors for the deposition of intermetallic phases (e.g. CrGa) by chemical vapor deposition.<sup>[4a]</sup> Analogous complexes with donor-free aluminum centers are very rare, and only two examples are known: [(Cp\*Al)<sub>2</sub>–(CpNi)<sub>2</sub>]<sup>[4b]</sup> and [{EtAl–CoCp\*(η<sup>2</sup>-C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>]<sub>2</sub>]<sup>[4c]</sup> in which the RAl<sup>I</sup> fragments have been described as CO-analogous two-electron bridging ligands. However, no quantum theoretical investigations of the bonding in these species have been carried out. Therefore, with this aim in mind, our interest was directed to the synthesis of a most simple structured model complex in which one donor-free RAl<sup>I</sup> unit is terminally bound to a transition metal fragment.

Treatment of a solution of [(Cp\*AlCl<sub>2</sub>)<sub>2</sub>]<sup>[5]</sup> in toluene with an excess of solid K<sub>2</sub>Fe(CO)<sub>4</sub> [Eq. (1)] gave a reaction mixture



whose IR spectrum, recorded after a short reaction time, exhibits the typical ν(CO) pattern for a pseudo-C<sub>3v</sub>-symmetric [LM(CO)<sub>4</sub>] complex. If the reaction is stopped at this stage, and the reaction solution is filtered and concentrated, complex **1** is obtained as colorless cubes in 10–20% yield by crystallization at –30 °C over several weeks. Attempts to increase the yield of **1** by employing other reaction media (THF, Et<sub>2</sub>O, CH<sub>2</sub>Cl<sub>2</sub>), phase-transfer reagents (R<sub>4</sub>N)(PF<sub>6</sub>); dibenzo-[18]crown-6), ultrasound, or higher temperature, have so far been unsuccessful.

The position of the <sup>27</sup>Al NMR signal at δ = –0.4 (w<sub>1/2</sub> = 2600 Hz) indicates that **1** differs considerably from donor-stabilized complexes of the type [L<sub>2</sub>Al(R)–M(CO)<sub>n</sub>]<sup>[4a]</sup> and resembles more closely the tetramer [(Cp\*Al)<sub>4</sub>]<sup>[2]</sup> whose Al nuclei are comparably shielded.<sup>[6]</sup> The single-crystal X-ray diffraction study<sup>[7]</sup> reveals that the Cp\*Al unit is indeed terminally bound (apical position) to the 16-electron Fe(CO)<sub>4</sub> fragment. The Al–Fe bond (223.1(3) pm) in **1** is significantly shorter than the Al–Fe bonds in typical Al<sup>III</sup> complexes such as [(<sup>t</sup>Bu){Me<sub>2</sub>N–(CH<sub>2</sub>)<sub>3</sub>}Al–FeCp(CO)<sub>2</sub>]<sup>[4d]</sup> (245.6(1) pm)<sup>[4d]</sup> and the Lewis acid/base adduct [(Ph)<sub>3</sub>Al–FeCp(CO)<sub>2</sub>]<sup>–</sup> (251.0(2) pm).<sup>[4e]</sup> In alloys (e.g. Al<sub>3</sub>Fe<sup>[4f]</sup>) the average Al–Fe distance (255 pm) is about 32 pm longer than in **1**. However, Al–M distances similar to those in **1** are found in multinuclear complexes with donor-free Al centers such as [(NiCp)<sub>2</sub>(Cp\*Al)<sub>2</sub>]<sup>[4e]</sup> (228 pm) and [{EtAl–CoCp\*(η<sup>2</sup>-C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>]<sub>2</sub>]<sup>[4f]</sup> (233 pm). The Al1–Fe1–C13 (87.8(3)°) and Al1–Fe1–C14 (82.1(2)°) angles (Fe–C14a is symmetrically equivalent; for atom numbering see Figure 1) are consistent with a weakly developed umbrella effect.<sup>[8]</sup> The Al1–Fe1–C12 angle (172.4(3)°) is close to the ideal value of 180° for a trigonal-bipyramidal coordinated Fe center. The average Al–C(Cp) distance (214.7 pm) is shorter than that in the Ni<sub>2</sub>Al<sub>2</sub> complex (225.3 pm) mentioned above; a value of 233.4 pm was found for the [(Cp\*Al)<sub>4</sub>] tetramer. Evidently, **1** exhibits a more pronounced charge polarization Al<sup>δ+</sup>–Cp<sup>δ–</sup>. However, an extreme description as a contact ion pair [Cp\*Al]<sup>2+</sup>[Fe(CO)<sub>4</sub>]<sup>2–</sup> can be ruled out on the basis of the position of the ν(CO) IR absorption bands (> 1900 cm<sup>-1</sup>) and the fact that Fe–Al coordination is preferred over isocarbonyl bridging Fe–C–O–Al.

Further information about the bonding was provided by quantum theoretical calculations using density functional theory in conjunction with relativistic pseudopotentials at Fe<sup>[9]</sup> on the model compound [(η<sup>5</sup>-Cp)Al–Fe(CO)<sub>4</sub>] (**1a**, substitution of Cp\* by Cp (C<sub>5</sub>H<sub>5</sub>)). The theoretical data for **1a** (Figure 2)