Inorg. Chem. **2007**, *46*, 11–13

Inorganic Chemistry Communication

Homo- and Heteroleptic Complexes of Four-Membered Group 13 Metal(I) N-Heterocyclic Carbene Analogues with Group 10 Metal(0) Fragments

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Received October 27, 2006

A series of complexes between recently developed four-membered group 13 metal(I) heterocycles and group 10 metal(0) fragments have been prepared and structurally characterized. One prepared complex, $[Pt\{Ga[N(Ar)]_2CNCy_2\}_3]$ (Ar = $C_6H_3Pr^i_2$-2,6; Cy = cyclohexyl), possesses the shortest Pt–Ga bonds yet reported, the covalent components of which are suggested by theoretical studies to have significant π character.

The coordination chemistry of group 13 metal(I) compounds is a rapidly emerging field. Most progress has been made with metal diyls, $:M^IR$ (R = bulky alkyl, aryl, $C_5Me_5^-$, etc.), which have been used in the formation of numerous complexes with p-, d-, and f-block metal fragments.[1] More recently, the coordination chemistry of the related anionic five-membered heterocycle, $[:Ga^I\{[N(Ar)C(H)]_2\}]^-$ (Ar = $C_6H_3Pr^i_2$-2,6), and neutral six-membered heterocycles, $[:M^I\{[N(Ar)C(Me)]_2CH\}]$ (M = Al or Ga), has begun to be explored, and analogies with both metal diyls and N-heterocyclic carbenes (NHCs) have been identified.[2] In 2006, we reported the synthesis of the first neutral four-membered group 13 metal(I) NHC analogues, $[:M\{[N(Ar)]_2CNCy_2\}]$ [M = Ga (**1**) or In (**2**), Cy = cyclohexyl].[3] Theoretical studies of models of the heterocycles suggested that they have a directional lone pair at the metal center (highest occupied molecular orbital, HOMO, of sp character) and thus the ability to act as σ donors. In addition, the metal centers each possess an empty p orbital (lowest unoccupied molecular orbital, LUMO), which could act as a π acceptor in transition-metal complexes. Although their HOMO−LUMO gaps are large (ca. 60 kcal/mol), they are less than those in the related six-membered heterocycles (ca. 100 kcal/mol).[2] Considering this and the fact that significant π back-bonding has been suggested in homoleptic group 13 diyl complexes of group 10 metals, e.g., $[Ni\{GaC(SiMe_3)_3\}_4]$,[1a,4] it was decided to examine the coordination of **1** and **2** toward group 10 metal(0) fragments. The aim here was to prove the σ-donor ability of **1** and **2** and to probe for metal−metal π bonding in homoleptic complexes of these ligands.[5] Such complexes would be of added interest because related homoleptic group 10 NHC complexes are finding applications in areas such as catalytic amination,[6] CO_2 fixation,[7] etc. Our preliminary results in this direction are reported herein.

The reactions of **1** and **2** with a range of group 10 olefin complexes were carried out (Scheme 1). The reaction of **1** with $[Ni(COD)_2]$ (COD = 1,5-cyclooctadiene) in either 2:1 or 4:1 stoichiometries afforded the heteroleptic complex **3** in good yield. Treatment of the Ni precursor with **2** at −80 °C led to deposition of Ni metal upon warming of the reaction mixture to −10 °C. The differences here are likely due to **2** being a poorer σ donor than **1** (higher s-character lone pair), which leads to instability of the In analogue of **3**, which is presumably formed in the reaction. In contrast, gallium and indium diyls can readily displace both ligands from $[Ni(COD)_2]$, and the resultant homoleptic complexes, $[Ni(ER)_4]$ (E = Ga or In), are kinetically inert.[1a,4] These differences are compatible with the greater steric bulk of **1** and **2** compared to metal diyls. The related Pt complexes, **4**

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(5) An Fe complex of a four-membered Ga heterocycle has been reported, but this was prepared via halide abstraction from an iron gallyl complex and contained a tetrahedral Ga center, thus precluding Fe−Ga π bonding. Jones, C.; Aldridge, S.; Gans-Eichler, T.; Stasch, A. *Dalton Trans.* **2006**, 5357.

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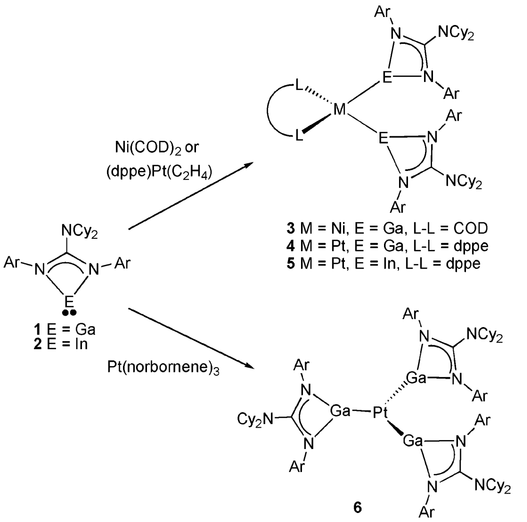
10.1021/ic062057d CCC: $37.00

Scheme 1. Syntheses of Compounds **3**−**6** (Ar = $C_6H_3Pr^i_2$-2,6; Cy = Cyclohexyl)



and **5**, were formed in low yields from the 2:1 reactions of the group 13 heterocycles with $[Pt(dppe)(C_2H_4)]$. Upon dissolution of isolated crystals of both complexes in toluene, decomposition to $[Pt(dppe)_2]$ and unidentified insoluble materials occurs. The instability of these complexes may result from loss of the bulky group 13 ligands in solution (vide infra). Similarly, the reactions of **1** or **2** with Pd(0) precursors, e.g., $[Pd_2(dba)_3]$ (dba = dibenzylideneacetone), resulted in Pd deposition below 0 °C.

More success was had in the 3:1 or 4:1 reactions of **1** with $[Pt(norbornene)_3]$, which in both cases gave the thermally stable homoleptic complex **6** in good yield. (N.B.: the 2:1 reaction led only to unidentified products.) Again, the related reactions with **2** led only to metal deposition at low temperature. Comparisons can be made between 3-coordinate **6** and monomeric, homoleptic Pt group 13 diyl complexes, which always possess 4-coordinate Pt centers in the solid state.[1a,4] Again, the greater steric bulk of **1** relative to diyl ligands can be used to explain this difference. It is of note that the aforementioned six-membered Ga(I) heterocycle has been used as a ligand toward Pt(0), but the only structurally characterized complex [Pt{Ga{[N(Ar)C(Me)]$_2$CH}}$_2$(η^2-1,3-COD)] is heteroleptic.[8]

The spectroscopic data for **3** and **6** are as would be expected for their proposed structures and will not be discussed here, except to comment that a number of the signals in the spectra of **6** are broad, presumably because of steric crowding of its bulky ligands (vide infra), which slow their rotation about the Pt−Ga bonds. The low solubility of this compound in normal solvents at low temperatures precluded a variable-temperature NMR study. Because of the instability of **4** and **5** in solution at ambient temperature and their poor solubility in noncoordinating solvents below 0 °C, no meaningful NMR data could be obtained for these complexes. Because these complexes were crystallized from toluene reaction solutions, which spent ca. 1 h at ambient temperature, they are apparently more stable in the presence of the slight excesses of **1** or **2** that were employed in these reactions. However, the room temperature $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture that gave **5** displayed only very broad peaks with no discernible ^{195}Pt satellites in the region 35−50 ppm. This indicates the presence of several products that are involved in one or more fluxional processes. The $^{31}P\{^1H\}$ NMR spectrum of the mixture that gave **4** also indicated several products, but a singlet at δ 39.9 ppm with ^{195}Pt satellites ($^1J_{PtP}$ = 3860 Hz) was assigned to this compound.

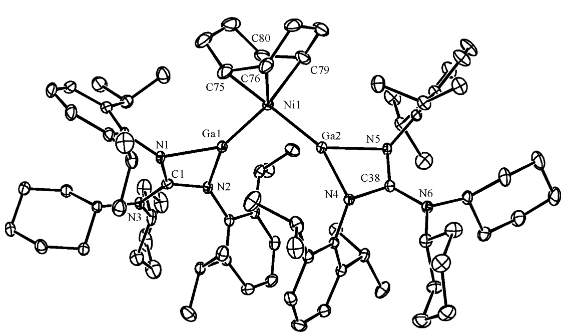


Figure 1. Molecular structure of **3** (H atoms removed for clarity). Selected bond lengths (Å) and angles (deg): Ga1−N2 2.047(3), Ga1−N1 2.060(3), Ga1−Ni1 2.2384(8), Ni1−C75 2.086(5), Ni1−Ga2 2.2401(9), Ga2−N4 2.041(3), Ga2−N5 2.066(3), N1−C1 1.354(5), C1−N2 1.356(5), C1−N3 1.364(5), N4−C38 1.361(5), N5−C38 1.346(5), N6−C38 1.374(5); N2−Ga1−N1 64.26(13), Ga1−Ni1−Ga2 103.74(4), N4−Ga2−N5 64.48(13), N1−C1−N2 107.4(3), N5−C38−N4 108.1(3).

The X-ray crystal structures[9] of **3**−**6** were obtained, and ORTEP diagrams for **3** and **6** are depicted in Figures 1 and 2. Those for **4** and **5** can be found in the Supporting Information, although relevant geometrical parameters are discussed here. The geometries of the heterocyclic ligands in **3** and **6** are similar to that of the free heterocycle,[3] although their Ga−N distances are slightly shorter and their N−Ga−N angles more obtuse, as would be expected upon coordination of the heterocycle. All compounds **3**−**5** have distorted tetrahedral geometries with M−M bond lengths (**3**, 2.319 Å mean; **4**, 2.357 Å mean; **5**, 2.533 Å mean) that lie within the known ranges for such interactions.[10] In accordance with the expected weaker donor ability of **2** compared to **1**, the

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(8) Mentioned as unpublished results in ref 1a.

(9) Crystal data for **3**·3THF: $C_{94}H_{148}Ga_2N_6NiO_3$, $M = 1608.33$, triclinic, space group $P\bar{1}$, $a = 13.496(3)$ Å, $b = 18.139(4)$ Å, $c = 18.576(4)$ Å, $\alpha = 80.05(3)°$, $\beta = 81.38(3)°$, $\gamma = 82.52(3)°$, $V = 4403.5(15)$ Å^3, $Z = 2$, $D_c = 1.213$ g cm^{-3}, $F(000) = 1736$, μ(Mo Kα) = 0.870 mm^{-1}, $T = 150(2)$ K, 15 373 unique reflections [R(int) 0.0499], R (on F) 0.0663, wR (on F^2) 0.1629 [$I > 2\sigma(I)$]. Crystal data for **4**·hexane: $C_{106}H_{150}Ga_2N_6P_2Pt$, $M = 1904.79$, triclinic, space group $P\bar{1}$, $a = 14.172(3)$ Å, $b = 17.635(4)$ Å, $c = 22.360(5)$ Å, $\alpha = 80.33(3)°$, $\beta = 88.13(3)°$, $\gamma = 68.81(3)°$, $V = 5134.3(18)$ Å^3, $Z = 2$, $D_c = 1.232$ g cm^{-3}, $F(000) = 1996$, μ(Mo Kα) = 1.957 mm^{-1}, $T = 150(2)$ K, 19 932 unique reflections [R(int) 0.1050], R (on F) 0.0721, wR (on F^2) 0.1451 [$I > 2\sigma(I)$]. Crystal data for **5**·0.5hexane: $C_{103}H_{143}In_2N_6P_2$-Pt, $M = 1951.90$, triclinic, space group $P\bar{1}$, $a = 15.690(3)$ Å, $b = 18.532(4)$ Å, $c = 19.397(4)$ Å, $\alpha = 102.36(3)°$, $\beta = 98.51(3)°$, $\gamma = 106.69(3)°$, $V = 5143.0(18)$ Å^3, $Z = 2$, $D_c = 1.260$ g cm^{-3}, $F(000) = 2018$, μ(Mo Kα) = 1.877 mm^{-1}, $T = 150(2)$ K, 17 969 unique reflections [R(int) 0.0451], R (on F) 0.0569, wR (on F^2) 0.1307 [$I > 2\sigma(I)$]. Crystal data for **6**·3toluene: $C_{132}H_{192}Ga_3N_9Pt$, $M = 2309.20$, monoclinic, space group $P2_1/n$, $a = 19.329(4)$ Å, $b = 33.357(7)$ Å, $c = 19.333(4)$ Å, $\beta = 96.36(3)°$, $V = 12389(4)$ Å^3, $Z = 4$, $D_c = 1.238$ g cm^{-3}, $F(000) = 4872$, μ(Mo Kα) = 1.821 mm^{-1}, $T = 150(2)$ K, 21 681 unique reflections [R(int) 0.0486], R (on F) 0.0345, wR (on F^2) 0.0761 [$I > 2\sigma(I)$].

(10) As determined from a survey of the Cambridge Crystallographic Database, Oct 2006.

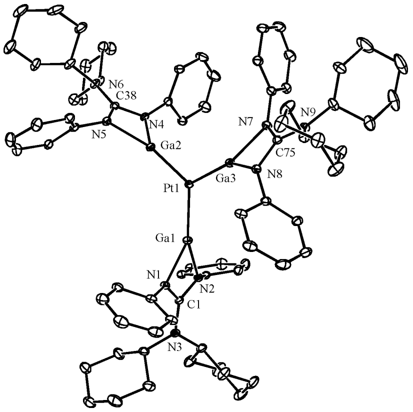

Figure 2. Molecular structure of **6** (H atoms and isopropyl groups removed for clarity). Selected bond lengths (Å) and angles (deg): Pt1−Ga2 2.3058(5), Pt1−Ga1 2.3108(6), Pt1−Ga3 2.3118(6), Ga1−N1 2.025(3), Ga1−N2 2.034(3), Ga2−N5 2.025(3), Ga2−N4 2.030(3), Ga3−N8 2.020(3), Ga3−N7 2.029(3), N1−C1 1.350(4), N2−C1 1.349(4), N4−C38 1.358(4), N5−C38 1.354(4), N7−C75 1.352(4), N8−C75 1.362(4); Ga2−Pt1−Ga1 119.47(2), Ga2−Pt1−Ga3 118.232(18), Ga1−Pt1−Ga3 122.295(14), N1−Ga1−N2 65.37(11), N5−Ga2−N4 65.78(11), N8−Ga3−N7 65.65(11), N2−C1−N1 108.6(3), N5−C38−N4 108.6(3), N7−C75−N8 108.0(3).

Pt−P distances in **5** (2.249 Å mean) are slightly shorter than those in **4** (2.261 Å mean).

The structure of **6** differs from the others in that it shows the complex to be homoleptic with a trigonal-planar Pt center. There appears to be considerable steric crowding between the heterocyclic ligands, two of which are nearly orthogonal to the trigonal plane (89.0° Ga1 heterocycle; 88.2° Ga2 heterocycle), while the other (Ga3 heterocycle) subtends an angle of 47.9° with it. This arrangement presumably relieves the congestion at the metal center. Despite this congestion, the Pt−Ga (3-coordinate) bond lengths (2.309 Å mean) are the shortest yet reported and can be compared to the next shortest bonds [Pt−Ga (2-ccordinate): 2.316 Å mean] in $[\mathrm{Pt(dcpe)\{GaC(SiMe_3)_3\}_2}]$ [dcpe = bis(dicyclohexylphosphino)ethane].[11] This, combined with fact that theoretical studies have suggested significant Pt−Ga π bonding (0.22 electrons versus the σ component, 0.19 electrons) in a model of the latter complex, encouraged us to carry out preliminary density functional theory (DFT) calculations on a model of **6**, viz., $[\mathrm{Pt\{Ga[N(C_6H_3Me_2\text{-}2,6)]_2CNMe_2\}_3}]$.

The optimized geometry of the complex closely resembles the structure of **6** in that two heterocyclic ligands are almost orthogonal to the coordination plane (angles between planes: 84.6° and 87.6°) while the third is not (angle between planes: 55.3°). The calculated Pt−Ga and Ga−N bond lengths (2.389 and 2.142 Å mean, respectively) are slightly longer (ca. 3%) than the experimental values, as is common for calculations of this type. To shed light on the nature of the short Pt−Ga bonds in **6**, a charge decomposition analysis (CDA) of the model complex was carried out. This technique has been used to quantify the σ (d) and π (b) components of metal−metal bonds.[4,12] In $[\mathrm{Pt\{Ga[N(C_6H_3Me_2\text{-}2,6)]_2CNMe_2\}_3}]$, the results indicate a significant (39.8% mean) π contribution to the Pt−Ga bonds. Similar π contributions to the M−E bonds in homoleptic diyl complexes, $[\mathrm{M(ER)_4}]$ (M = Ni, Pd, or Pt; E = B−Tl), have been calculated by CDA and other methods and were said to be significant.[1a,4,13] It should be noted, however, that this fraction only relates to the covalent components [d, 0.43 electrons (mean); b, 0.29 electrons (mean)] of the Pt−Ga bonds, which are polarized (atomic charges: Pt, −0.96; Ga, +0.44) and thus have a considerable electrostatic component. An orbital population analysis of the model suggested that the majority of the π contribution to the Pt−Ga bonds is derived from the bonding combination of two nearly degenerate Ga empty p-orbital sets (mixed with Ga lone pair sets of appropriate symmetry) with either the Pt d_{xy} or $d_{x^2-y^2}$ orbitals, giving rise to HOMO and HOMO−1, respectively (Figure 3). The antibonding combination of these orbitals comprise the LUMO+1 and LUMO+2.

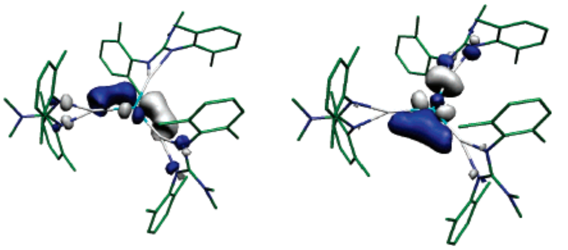

Figure 3. Representations of (a) the HOMO (−0.1394 hartrees) and (b) the HOMO−1 (−0.1411 hartrees) of $[\mathrm{Pt\{Ga[N(C_6H_3Me_2\text{-}2,6)]_2CNMe_2\}_3}]$.

In summary, we have prepared and structurally characterized a series of group 10 metal(0) complexes with four-membered Ga(I) and In(I) heterocycles. Crystallographic and theoretical studies suggest that the covalent components of the Pt−Ga bonds in one homoleptic complex possess significant π character. Considering the synthetic applications that homoleptic group 10 NHC complexes are finding, we are currently examining further related chemistry of complexes such as **6** and will report on this in due course.

Acknowledgment. We gratefully acknowledge financial support from EPSRC in the form of a partial studentship for S.P.G.

Supporting Information Available: Crystallographic CIF files for **3**−**6**, ORTEP diagrams for **4** and **5**, full synthetic details for **3**−**6**, spectroscopic data for **3** and **6**, and full details of the DFT calculation. This material is available free of charge via the Internet at http://pubs.acs.org.

IC062057D

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