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Reversible Addition of Alkynes to Gallium Complex of Chelating Diamide Ligand

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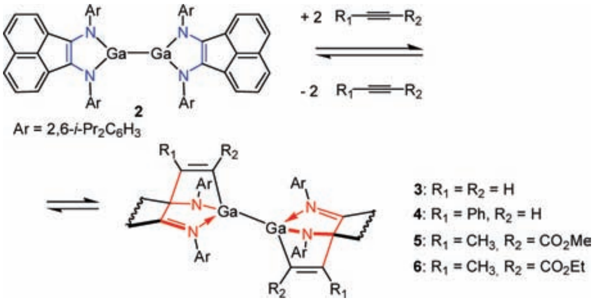
Spectacular application of transition metal complexes as catalysts in organic synthesis is ensured by two distinct features of transition metal ions: *(i) ability to coordinate unsaturated organic molecules* and *(ii) ability to exist in several, easily interchanging, oxidation states*. The latter makes oxidative addition and reductive elimination possible at a single transition metal center. A lack of these features sets the main group metals beyond catalytic applications that are observed for transition metals. However, s- and p-block metal complexes that emulate reactivity of transition metal complexes can be made using noninnocent ligands. In that context complex (dpp-Bian)Mg(thf)$_3$ (**1**) (dpp-Bian = 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene) is an illustrative example. It exhibits manifold reactivity toward different substrates.[1] In the course of reactions of complex **1** the electronic configuration, geometry, and functionality of dpp-Bian ligand undergo dramatic changes. As reactivity of transition metal complexes can be "tuned" by changing the nature of the spectator ligands, the variation of the metal ion bound to dpp-Bian dianion may affect a course of its reactivity. Here, we report a facile addition of alkynes to a gallium complex, successful structural and spectroscopic characterization of the addition products, and unusual thermally induced elimination of the alkyne accompanied by C–C and C–Ga bond cleavage.

Treatment of toluene solution of **2** with $HC{\equiv}CH$, $PhC{\equiv}CH$, or $MeC{\equiv}CCO_2R$ (R = Me, Et) at $T < 293$ K caused an instant color change from deep-blue to red (Scheme 1).

Products **3**, **4**, **5**, and **6** have been isolated as red crystals by the room temperature crystallization from Et_2O (**3**), dme (**4**), and benzene (**5**, **6**), and they have been characterized by IR and ^{1}H NMR spectroscopy as well as by the single crystal X-ray analysis. Molecular structures of **4** and **6** are depicted in Figures 1 and 2 respectively; the main bond lengths in **3**–**6** are given in Table 1.

The structures of **3**–**6** reveal that in each case the alkyne adds across the Ga–N–C fragment resulting in carbon–carbon and carbon–gallium bonds. In the transition metal chemistry there is a sole example of related isolable compound. It was produced in the reaction of $MeO_2CC{\equiv}CCO_2Me$ (very strong π-accepting alkyne) with $[{}^tBuN{=}C(H){-}C(Ph){=}O]Fe(CO)(dppe)$.[2] Frühauf et al. have shown that reactions of Fe, Ru, Mn complexes of 1,4-diaza-1,3-diene (dad) with reagents possessing multiple carbon-element bonds often proceed with formation of kinetically unstable [2+3] cycloadducts.[3] However, toward less active substrates, e.g. $PhC{\equiv}CH$ and $HC{\equiv}CH$, the transition metal–dad complexes are unreactive. Structurally characterized cycloaddition products have been also prepared by reacting aromatic ketones with Zr[4a] and Sm[4b] dad complexes. Iridium[5a] and rhodium[5b] catecholates add dioxygen across an M–O–C segment to give isolable endoperoxides. In coordination chemistry of the main group metals an only example of such cycloaddition is binding of dioxygene by triphenylstibiumcatecholate and -amidophenolate species.[5c,d,e] Just recently reversible addition of $H_2C{=}CH_2$ to $Sn{\equiv}Sn$ bond in Ar_2Sn_2 has been reported.[6] Alkenes and alkynes add irreversibly to aluminum β-diketiminates across the 1,4-position.[7]

Scheme 1. Reactions of **2** with Alkynes[a]



[a] Naphthalene rings are omitted except of complex **2**.

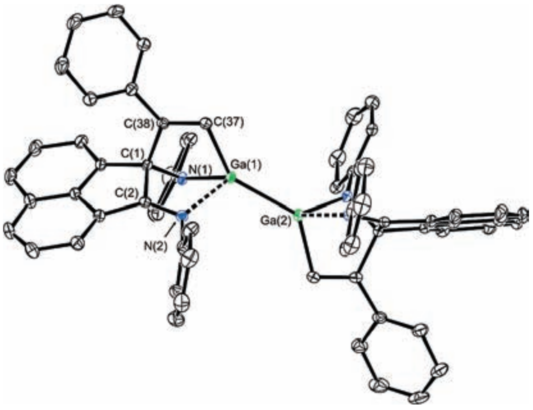


Figure 1. Molecular structure of **4** (H atoms and *i*Pr groups are omitted).

Increase of a coordination number of gallium atoms from three to four on going from **2** to **3**–**6** causes elongation of the Ga–Ga bond in the products **3**–**6** (Table 1) compared to that in **2** (2.3598(3) Å).[8] Cycloaddition of alkynes across the Ga–N–C fragment in **2** makes C(1) and Ga(1) atoms in **3**–**6** chiral, thus resulting in four asymmetric centers in dinuclear molecules. In the crystals, complexes **3** and **4** are represented as C-homochiral dimers (two pairs of *R,R* and *S,S* enantiomers), whereas the unit cell of compound **6** consists of only a heterochiral dimer. Complex **5** represents the third case: two pairs of *R,R* and *S,S* enantiomers (C-homochiral dimers) as well as their diastereomer (*R,S*) are simultaneously present in the unit cell.

A marked difference in the Ga–N bond lengths (Table 1) within each matallacycle in **3**–**6** reflects the amido/imino character of the N-chelating fragment. Slightly distorted trigonal planar environ-

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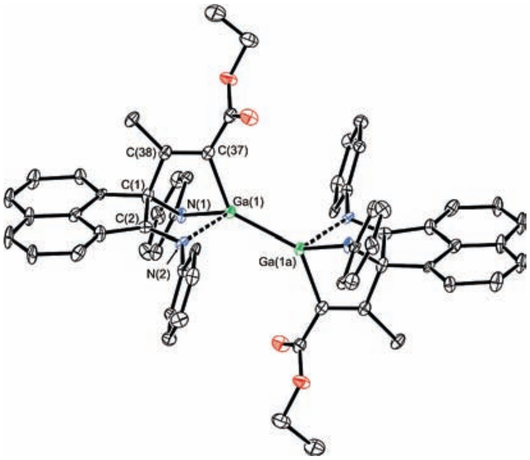

Figure 2. Molecular structure of **6** (H atoms and *i*Pr groups are omitted).

Table 1. Selected Bond Lengths (Å) in Complexes **3**, **4**, **5**, and **6**

	3[a]	**4**	**5**[a,b]	**6**
Ga(1)−Ga(2)	2.4067(4)	2.4052(3)	2.416(1)	2.419(1)
Ga(1)−N(1)	1.929(2)	1.926(1)	1.904(3)	1.913(5)
Ga(1)−N(2)	2.190(2)	2.173(1)	2.203(3)	2.193(5)
Ga(1)−C(37)	1.994(3)	1.988(1)	2.015(4)	2.020(6)
N(1)−C(1)	1.481(3)	1.476(2)	1.465(5)	1.463(7)
N(2)−C(2)	1.280(3)	1.280(2)	1.272(5)	1.282(7)
C(1)−C(2)	1.550(3)	1.554(2)	1.556(6)	1.556(8)
C(1)−C(38)	1.551(3)	1.575(2)	1.574(6)	1.568(8)
C(37)−C(38)	1.316(3)	1.336(2)	1.333(6)	1.335(7)

[a] The atom labeling is the same as in Figure 1. [b] For heterochiral dimer.

ments of the atoms C(37) and C(38) are credited to their sp^2 nature, and the C(37)−C(38) bond lengths in **3**−**6** (1.316(3)−1.336(2) Å) correspond perfectly to the double bonds. The newly formed C(1)−C(38) bonds (1.551(3)−1.575(2) Å) are just slightly longer than the typical single C−C bond (1.54 Å). The Ga−C(37) bonds (1.988(1)−2.020(6) Å) are well compared with those in vinyl derivatives $[(CH_2{=}CH)_2Ga(\mu\text{-}PBu^t{}_2]_2$ (1.95(2) and 1.96(2) Å)[9a] and 1,4-$C_6H_4[HC{=}C(SiMe_3)GaBu^t{}_2]_2$ (1.974(4) Å).[9b]

With the normal lengths of the newly formed carbon−carbon and carbon−gallium bonds considered, elimination of alkynes from **3**−**6**, which is observed at elevated temperatures, is rather surprising. In solution a complete conversion of **3** and **4** to the initial digallane **2** and the corresponding alkyne takes place at temperatures below 100 °C, whereas with butynoate adducts **5** and **6** it requires heating to *ca.* 200 °C. In the case of **3** and **4** the alkyne elimination processes have been monitored by absorption spectroscopy. At +10 °C the spectrum of **4** in toluene (Figure 3) exhibits absorption at 352 nm, which decreases with the temperature rising. Concurrently the absorption at 585 nm, which indicates the formation of complex **2**,[7] is increasing. At the temperature above +70 °C the spectral picture remains unchanged, thus signifying a full conversion of **4** to the starting materials. The elimination processes are reversible in solution for all four addition products. However, refluxing of solutions of **3** and **4** for tens of hours or standing solutions at ambient temperatures for more than one month lead to transformation of the alkynes to unidentified products and regeneration of complex **2**, which is stable in solution for an indefinite period of time.

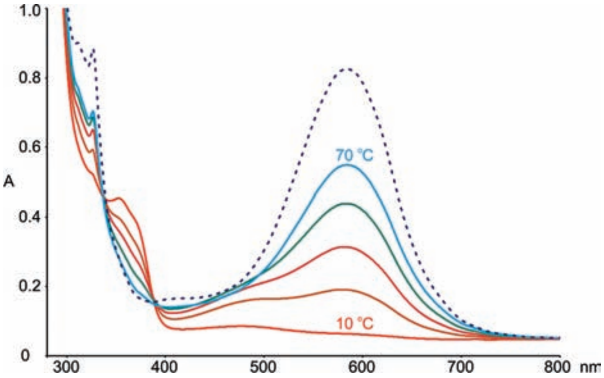

Figure 3. Variable-temperature absorption spectra of **4** in toluene (solid lines). The absorption spectrum of **2** in toluene at 293 K (dashed line).

In summary, we have shown that alkynes can undergo reversible addition to the main group metal complex. The gallium diimine complex **2** is exceptionally selective toward alkynes and does not react with other substances having multiple bonds, for example, Me(H)C═C(H)CO$_2$Me, Me$_2$C═O, RC≡N (R = Me, Ph), PhN═C, etc. Among the possible mechanisms of the alkyne addition to complex **2**, a concerted process seems to be the most plausible one. The influence of electronic factors on regioselectivity of the addition reaction is evident from the fact that a bulkier substituent at the triple C−C bond in the case of **3** (Ph group) is oriented away from the metal, whereas in the case of **5** and **6** (ester group) it would be oriented toward the metal. We believe that the observed reactivity of complex **2** may be exploited in catalysis. We have already shown that **2** catalyzes hydroamination of PhC≡CH with 4-chloraniline: with 2 mol % of **2** in toluene 99% conversion of the reagents was achieved within 6 h at 110 °C. Mononuclear Ga and Al dpp-Bian complexes' behavoir toward alkynes is similar to that of **2**. A study of their reactivity is in progress.

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Supporting Information Available: Spectroscopic and analytical data for **3**−**6** including crystal data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Fedushkin, I. L.; Khvoinova, N. M.; Skatova, A. A.; Fukin, G. K. *Angew. Chem.* **2003**, *115*, 5381–5384; *Angew. Chem., Int. Ed.* **2003**, *42*, 5223−5226. (b) Fedushkin, I. L.; Makarov, V. M.; Rosenthal, E. C. E.; Fukin, G. K. *Eur. J. Inorg. Chem.* **2006**, 827–832. (c) Fedushkin, I. L.; Nikipelov, A. S.; Skatova, A. A.; Maslova, O. V.; Lukoyanov, A. N.; Fukin, G. K.; Cherkasov, A. V. *Eur. J. Inorg. Chem.* **2009**, 3742–3749. (d) Fedushkin, I. L.; Skatova, A. A.; Hummert, M.; Schumann, H. *Eur. J. Inorg. Chem.* **2005**, 1601–1608.

(2) Siebenlist, R.; Frühauf, H.-W.; Vrieze, K.; Smeets, W. J. J.; Spek, A. L. *Organometallics* **2002**, *21*, 5628–5641.

(3) Frühauf, H.-W. *Coord. Chem. Rev.* **2002**, *230*, 79–96.

(4) (a) Scholz, J.; Görls, H. *Inorg. Chem.* **1996**, *35*, 4378–4382. (b) Scholz, J.; Görls, H.; Schumann, H.; Weimann, R. *Organometallics* **2001**, *20*, 4394–4402.

(5) (a) Barbaro, P.; Bianchini, C.; Mealli, C.; Meli, A. *J. Am. Chem. Soc.* **1991**, *113*, 3181–3183. (b) Dutta, S.; Peng, S.-M.; Bhattacharya, S. *Inorg. Chem.* **2000**, *39*, 2231–2234. (c) Abakumov, G. A.; Poddel'sky, A. I.; Grunova, E. V.; Cherkasov, V. K.; Fukin, G. K.; Kurskii, Y. A.; Abakumova, L. G. *Angew. Chem.* **2005**, *117*, 2827–2831; *Angew. Chem., Int. Ed.* **2005**, *44*, 2767−2771. (d) Abakumov, G. A.; Cherkasov, V. K.; Grunova, E. V.; Poddel'skii, A. I.; Abakumova, L. G.; Kurskii, Yu. A.; Fukin, G. K.; Baranov, E. V. *Dokl. Chem.* **2005**, *405*, 222–225. (e) Cherkasov, V. K.; Abakumov, G. A.; Grunova, E. V.; Poddel'sky, A. I.; Fukin, G. K.; Baranov, E. V.; Kurskii, Y. V.; Abakumova, L. G. *Chem.−Eur. J.* **2006**, *12*, 3916–3927.

(6) Peng, Y.; Ellis, B. D.; Wang, X.; Fettinger, J. C.; Power, P. P. *Science* **2009**, *325*, 1668–1670.

(7) Ariafard, A.; Lin, Z.; Jordan, R. F. *Organometallics* **2005**, *24*, 5140–5146.

(8) Fedushkin, I. L.; Lukoyanov, A. N.; Ketkov, S. Y.; Hummert, M.; Schumann, H. *Chem.−Eur. J.* **2007**, *13*, 7050–7056.

(9) (a) Culp, R. D.; Cowley, A. H.; Decken, A.; Jones, R. A.; Bond, M. R.; Mokry, L. M.; Carrano, C. J. *Inorg. Chem.* **1997**, *36*, 5165–5172. (b) Uhl, W.; Bock, H. R.; Breher, F.; Claesener, M.; Haddadpour, S.; Jasper, B.; Hepp, A. *Organometallics* **2007**, *26*, 2363–2369.

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