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Adaptive Behavior of Redox-Active Gallium Carbenoid in Complexes with Molybdenum†‡

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Gallium(I) carbenoid derived from redox-active diimine 1,2-bis(2,6-diisopropylphenyl)iminoacenaphthene (dpp-bian) in complexes with molybdenum may serve either as neutral [dpp-bian]Ga• or anionic [dpp-bian]Ga•– two-electron donor depending on electronic state of the transition metal.

First anionic 1,3,2-imidazagalol (structure A, Scheme 1), namely [(tBuNCH)2]Ga, has been reported by Schmidbaur and co-workers in 1999. During the following decade, the chemistry of the related anion [(DAB)Ga•] [DAB = (2,6-IPrC6H3NCH)2] was intensively studied by Jones and co-workers. They succeeded in preparing complexes of [(DAB)Ga•] for most of the metals of the Periodic Table, thus proving the versatility of [(DAB)Ga•] as Ga-donor ligand. Anionic 1,3,2-imidazagalols are isoelectronic with neutral N-heterocyclic germylenes (structure C, Scheme 1). The latter compounds are the heavier analogues of Arduengo’s carbenes, which now represent one of the most useful class of ligands. While the existence of radical species like D (Scheme 1) is proven, neutral radicals of type B were neither observed as coordinated ligands nor as free species. Interestingly, radical R2Ga• (R = (2,6-IPrC6H3NCH)2) has been recently reported.

The reaction between (dpp-bian)Ga–Ga(dpp-bian) and an excess of Mo(CO)6 proceeds in tetrahydrofuran (THF) at 100 °C (sealed glass ampoule). Within 15 hours, the reaction mixture turns from deep blue to green. The removal of the excess carbonyl reagent by sublimation and crystallisation of the product from benzene gives green crystals of (dpp-bian)Ga–Mo(CO)5 (2) in 95 % yield (Scheme 2). A lack of signals in the 1H NMR spectrum of compound 2 suggests its paramagnetic character. Indeed, EPR spectroscopy proves the presence of an unpaired electron in complex 2. The interaction between compound 1 and [CpMo(CO)5]2 also proceeds in THF, but under less drastic conditions (80 °C, 1 h) compared to compound 2. The diamagnetic product (dpp-bian)Ga–Mo(CO)5Cp (3) was obtained in form of dark brown crystals (93 %) from 1,2-dimethoxyethane (Scheme 2). Reduction of compound 1 with two equivalents of sodium in THF resulted (in situ) in (dpp-bian)Ga–Na(THF)2, which reacts with Mo(CO)6 in THF at 25 °C within 1 h to give green carbonylate [(dpp-bian)Ga–Mo(CO)5]Na(THF)2]2 (4) (97 %) (Scheme 2).

Here we report for the first time the generation (in situ) of a heterocyclic radical [(dpp-bian)Ga•] (dpp-bian = 1,2-bis(2,6-diisopropylphenyl)iminoacenaphthene), which is rather stable when coordinated to a transition metal, e.g. molybdenum. On the other hand, we show here that, if required, electrons can be transferred from the transition metal centre to this radical, thus providing the formation of a gallen-anion. The interplay between [(dpp-bian)Ga•] and [(dpp-bian)Ga•] is needed to ensure the stability of the 18 electron configuration at the transition metal.

Scheme 1 N-Heterocyclic gallium and germanium carbenoids.

Scheme 2 Syntheses of the compounds 2, 3, and 4.

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Compounds 2-4 are thermally quite robust: decomposition of crystalline samples takes place above 200 °C. The EPR signal of a solution of compound 2 (Figure 1) reveals a hyper-fine splitting (hfs) due to coupling of the unpaired electron with two pairs of protons, two equivalent ¹⁴N nuclei and the two magnetic gallium isotopes, ⁶⁹Ga (60.11 %) and ⁷¹Ga (39.89 %). The EPR spectrum unequivocally indicates the presence of the heterocyclic radical [(dpp-bian)Ga] in complex 2. This radical acts as a two-electron neutral σ-donor towards molybdenum, thus, providing the 18 electron configuration of the transition metal centre together with the five CO ligands. At that stage, we cannot conclude whether the back donation from molybdenum to unoccupied pₓ orbital of gallium takes place. Alternatively, this orbital might be populated with lone pairs of the nitrogen atoms. Note, that in THF compound 2 exhibits thermochromism (green and red at ambient and low temperature, correspondingly). It seems to be reasonable to suggest that this phenomenon reflects the coordination of the solvent donor molecule to the empty gallium p orbital because not color alteration has been observed in non-coordinating solvent like toluene.

The Ga–Mo bonds in complexes 2, 3, and 4 are very much alike (2: 2.5352(3); 3: 2.5608(4); 4: 2.5678(3) Å) and can be compared with those bonds in (Cp*Ga)₆Mo (2.3844(6)-2.4930(7)Å), (Cp*Ga)₆Mo(CO)₄ (2.5188(8)-2.5228(8) Å), (Cp*Ga)₃Mo(CO)₄ (2.537(1) and 2.554(1) Å) and (CpMo(CO)₂[(Gal)(OH)] (L = [N(2,6-iPr₂C₆H₃)]₂CN(C₆H₁₁)₂) (2.5728(9) and 2.5896(9) Å). Compounds 3 and 4 are diamagnetic: their ¹H NMR spectra reveal the expected signals for the dpp-bian ligands. Thus, in complex 3 the isopropyl groups in dpp-bian give rise to two doublets (δ 1.34 and 1.15 ppm), and one septet (δ 3.83 ppm). The cyclopentadienyl protons in 3 result in a singlet at δ 4.40 ppm. The molecular structures of compounds 2, 3, and 4 were determined by single crystal X-ray diffraction, and are depicted in Figures 2, 3, and 4 respectively. Compound 2 and 4 represent octahedral Mo(0) d₆ complexes. Although the Mo–CO bonds in compound 2 lie within a narrow range (1.999(3)-2.042(2) Å), it is worth to mention, that the CO ligand trans-positioned to gallium exhibits the shortest bond to molybdenum. One might assume a weak back donation from the transition metal to the gallium in compound 2. In complex 4 the Mo–CO bonds (2.004(1)-2.060(2) Å) are very similar to those in compound 2. Compound 3 has a “four-leg piano stool geometry” and can be viewed as a molybdenum gallyl with a Ga–Mo covalent bond. The electron count for compound 3 indicates a 18 electron Mo(II) d₆ complex. As in compounds 2 and 3, the Mo–CO bonds lengths in complex 3 are close to each other (1.977(3)-2.004(4) Å).
Structural "fingerprint". While evolving from the neutral, to the reduced heterocyclic gallium carbenoids, every reduction state of dpp-bian has its own characteristic complexes of heterocyclic gallium carbenoids. In the case of compound [Ni(dpp-bian)P2C6H3NCH)2], the C–N bonds of the benzene ring are shorter.14 In complex [Ni(dpp-bian)P2C6H3NCH)2], the C–N bonds are sensitive to the electronic configuration of the coordination centre.25 The crystal data for [Ni(dpp-bian)P2C6H3NCH)2], the C–N bonds of the benzene ring are shorter.14 In complex [Ni(dpp-bian)P2C6H3NCH)2], the C–N bonds are sensitive to the electronic configuration of the coordination centre.25 Noteworthy, an attempted synthesis of the analogue of compound [Ni(dpp-bian)P2C6H3NCH)2] failed.13

The most significant difference between molecules 2 and 4 is related to the geometries of the gallium heterocycles. Every reduction state of dpp-bian has its own structural "fingerprint". While evolving from the neutral, to the reduced heterocyclic gallium carbenoids, every reduction state of dpp-bian has its own characteristic complexes of heterocyclic gallium carbenoids. In the case of compound [Ni(dpp-bian)P2C6H3NCH)2], the C–N bonds of the benzene ring are shorter.14 In complex [Ni(dpp-bian)P2C6H3NCH)2], the C–N bonds are sensitive to the electronic configuration of the coordination centre.25 Noteworthy, an attempted synthesis of the analogue of compound [Ni(dpp-bian)P2C6H3NCH)2] failed.13

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