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Carbene Complexes

Unusual Tilted Carbene Coordination in Carbene Complexes of Gallium(I) and Indium(I)**

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First attempts to isolate carbenes date back to the early 19th century,[1] and interest increased throughout the 20th century,[2,3] but research and application of these subvalent carbon ligands did not really rise prior to the preparation of isolable and storable N-heterocyclic carbenes (NHCs). In the two decades since the publication of the first stable crystalline carbene by Arduengo et al.,[4] carbenes have evolved from mere reaction intermediates in biological or industrial processes to quintessential ligands in modern coordination chemistry[5] and catalysis.[6,7] NHCs are most well-known for their ability to coordinate transition metals,[8,9] but a good number of main-group complexes have also been reported.[8,10–12] Among those are a number of gallium(III)[10,13] and indium(III)[14,15] complexes, but no such compounds are known for gallium(I) and indium(I) to date. Previous attempts have led to the formation of dimerized M^{II} species.[16,17] This may be prevented by the use of suitable starting material. In this context we established a simple route to weak complexes of solvated $[M^I(arene)_{2,3}]^+[Al(OR^F)_4]^-$ (M = Ga, In).[18–20] Those are versatile precursors for coordination chemistry, for example, complexes with phosphanes and crown ethers.[18,19,21] NHCs are known to mimic phosphanes in their ability to form strong σ-bonds but only weak π-bonds to metal centers.[22] They have in fact outperformed and replaced phosphanes in many applications.[7] Therefore, we now expand the coordination chemistry of gallium(I) and indium(I) to NHCs.

A yellow solution formed when $Ga^+[Al(OR^F)_4]^-$ was dissolved in fluorobenzene together with two equivalents of 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr). The characteristic NMR signals of the $[Al(OR^F)_4]^-$ anion were observed in this solution ($\delta(^{19}F) = -74.9$ ppm; $\delta(^{27}Al) = 33.8$ ppm).[23] The ^1H NMR spectrum displayed signals that are reasonably close to reported shifts of the IPr ligand,[24] but with a considerably upfield-shifted signal for the methine proton of the isopropyl group (2.19 vs. 2.96 ppm). This is in agreement with the spectra of similar complexes with transition metals.[25,26] Unlike in the bare starting material, no signal was observed in the ^{71}Ga NMR spectrum, which is a similar situation to the gallium phosphane complexes. This is interpreted as an indication of the complexation of the Ga^+ cation by the carbene.[18,19,27]

Crystallization of the yellow Ga^+/IPr solution by concentration and storage at −40 °C yielded crystals that analyzed as $[Ga(IPr)_2]^+[Al(OC(CF_3)_3)_4]^-\cdot PhF$ (**1**; Figure 1 a). Much like in the complexes with bulky phosphane ligands such as $PtBu_3$,[18] the central gallium ion is coordinated in a bent fashion with an angle of 118.2° ($d_{Ga-C} = 229$ pm).

The coordination is in fact not ideal, as the donation of electron density from carbon into the empty p orbitals of gallium would benefit from a much smaller angle (compare the gallium(I) phosphane complexes).[18,19] The gallium(I) ion is also not in plane with either ring. Figure 1 b presents the

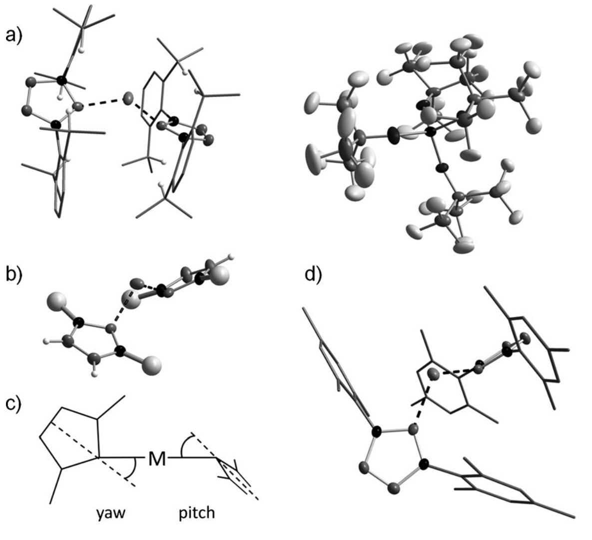

Figure 1. a) Molecular structure of **1**. The bulky substituents of the NHC are shown as wire models. Hydrogen atoms have been omitted for clarity, except for the methine protons, which are discussed in the NMR section. b) Simplified representation of the coordination environment at Ga^+ in **1**. The bulky substituents are represented by the large spheres. c) Illustration of the pitch and yaw angles of the NHC coordination at a metal cation.[28] d) Molecular structure of the $[Ga(IMes)_2]^+$ cation of **3**. Structural details of **1**, **2**, and **3** are included in Table 2. Ellipsoids are set at 50% probability.

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slightly tilted position of the ligands more clearly. At first sight, this tilt appears to be forced by a compromise of 1) close contact from ligand to metal and preferably small coordination angle with 2) the high steric demand of the NHC ligand. Such effects have occasionally been reported for complexes of main-group metals and more rarely for transition metals.[28–31] The tilt is quantified by the offset angle of the M−C bond to the C_2 axis of the NHC, which is split into pitch and yaw angles for better understanding of the underlying effects (Figure 1 c).

Table 1: Calculated gas-phase ligand exchange reactions at BP86/def-SV(P) and *B3LYP/def2-TZVPP* levels.[a]

Reaction	ΔH_{rxn}(Ga)	ΔH_{rxn}(In)
1 a) $[M(PhF)_2]^+ + TMI \rightarrow [M(TMI)]^+ + 2\,PhF$	−105/*−109*	−95/*−97*
1 b) $[M(PhF)_2]^+ + PPh_3 \rightarrow [M(PPh_3)]^+ + 2\,PhF$	−14/*−29*[18]	−13/*−30*[18]
2 a) $[M(PhF)_2]^+ + 2\,TMI \rightarrow [M(TMI)_2]^+ + 2\,PhF$	−278/*−250*	−251/*−218*
2 b) $[M(PhF)_2]^+ + 2\,PPh_3 \rightarrow [M(PPh_3)_2]^+ + 2\,PhF$	−110/*−109*[18]	−96/*−99*[18]
3 a) $[M(PhF)_2]^+ + 3\,TMI \rightarrow [M(TMI)_3]^+ + 2\,PhF$	[b]	[b]
3 b) $[M(PhF)_2]^+ + 3\,PPh_3 \rightarrow [M(PPh_3)_3]^+ + 2\,PhF$	−162/*−141*[18]	−147/*−134*[18]

[a] Enthalpies at RT are given in $kJ\,mol^{-1}$. The values for the corresponding triphenylphosphane complexes are given for comparison. [b] No minimum energy structure was found for this coordination mode, which is most likely due to steric reasons.

Yaw angles are sometimes observed owing to steric crowding and they do not affect the binding mode fundamentally. The more striking observations are the extremely large pitch angles. To our knowledge, pitch angles as high as these have hitherto never been reported for unsupported carbene complexes. However, in some cases with chelating carbenes, similar values were reported.[32] Aldridge and Jones recently reported bent boryl complexes of Si^{II}, Ge^{II}, and Sn^{II}; for example, $Sn\{B(NArCH)_2\}_2$, which is isostructural and isoelectronic to complex **2**$^+$ that strikingly displays pitch angles of up to 18°.[33] It can also be noticed from the crystal structure of **1** that all methine protons of the isopropyl groups are pointing inwards, somewhat in the direction of the imidazole rings. This explains the strong sensitivity (upfield shift) of the corresponding signal in the ^{1}H NMR spectrum to coordination.[25,26]

Entirely analogous complexes were obtained by treating $In^+[Al(OC(CF_3)_3)_4]^-$ with IPr, giving $[In(IPr)_2]^+[Al(OC(CF_3)_3)_4]^-$ (**2**), and $Ga^+[Al(OR^F)_4]^-$ with two equivalents of 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes) giving $[Ga(IMes)_2]^+[Al(OC(CF_3)_3)_4]^- \cdot 0.5\,PhF$ (**3**).[34] The structural details of complexes **1** and **2** are summarized and compared in Table 2. The distance d_{M-C} for In is about 20 pm longer than for Ga (compare with the 27–29 pm difference found for Sn−P in the phosphane complexes).[18] The C-In-C coordination angle is essentially identical to the Ga system, while the tilt angles are slightly larger. The structure of **3** is shown in Figure 1 d and the structural details are summarized in Table 1 along with the IPr complexes. The approximately 10 pm shorter d_{Ga-C}, if compared to the IPr complex, and the considerably smaller C-Ga-C coordination angle are directly ascribed to the lower steric demand of the ligand. The less-pronounced tilting of the NHC-rings may also stem from the decreased steric demand. Attempts to crystallize the homologous indium structure were unsuccessful.

Table 2: Comparison of the structural details of Ga^I and In^I carbene complexes. Experimental values of **1**, **2**, and **3** are given in comparison to TMI model complexes computed at the BP86/def-SV(P) level.[a]

	M-C	(C-M-C)	N-C-N	Charge (M)		θ_{pitch}	θ_{yaw}
				PABOON	NPA		
1	229	118.2(1)	102.7	–	–	29.4	11.4
2	250	120.8	103.1	–	–	32.8	11.5
3	219	104.5(1)	104.0	–	–	22.6	12.7
$[Ga(TMI)]^+$	221.1	–	104.8	0.335	0.795	0.0	0.0
$[Ga(TMI)_2]^+$	221.2	96.94	104.1	−0.143	0.585	19.4	4.7
$[In(TMI)]^+$	241.6	–	103.9	0.333	0.834	0.0	0.0
$[In(TMI)_2]^+$	243.8	93.01	103.9	−0.147	0.666	17.9	3.7
$[Ga(H)(TMI)]$	222.8	–	103.8	−0.411	0.309	12.4	5.0
$[Ga(TMI)(CO)]^+$	220.4	90.44	105.0	0.177	0.705	7.1	1.1

[a] Selected distances are given in pm, selected angles are given in °. Average values are given where appropriate.

The much smaller NHC 1,3,4,5-tetramethylimidazol-2-ylidene (TMI) was chosen as a model system for the much more economical computing time in comparison to the large bulky systems used in the experiments. Attempts to analyze the structure of the gallium(I) TMI complex experimentally failed in our hands. For comparison to earlier work,[18,21] the ligand exchange was investigated at the BP86/def-SV(P) and B3LYP/def2-TZVPP levels (Table 1).

The overall trends found for the phosphane complexes are confirmed here: The exchange of fluorobenzene is favored even for the first ligand, but is much more exothermic for two ligands. The values for indium are slightly smaller than for gallium, but roughly in the same range. Compared to the phosphane reactions, the carbene reactions were found to be up to 155 $kJ\,mol^{-1}$ more exothermic in our calculations. This confirms the superior donor quality of carbenes compared to phosphanes.[22,35] However, while Ga^I and In^I can bind a less-demanding phosphane like PPh_3 three times, this does not appear to be possible even for the small model carbene TMI owing to steric or possibly also electronic reasons, because of the stronger donor ability of TMI and thus reduced acceptor capacity of the metal (see partial charges M in Table 2).

The basic coordination Scheme in the bis(carbene) complexes is illustrated by the graphic representation of the frontier orbitals of the $[Ga(TMI)_2]^+$ complex (see the Supporting Information): The HOMO is essentially the s orbital at gallium, while the LUMO has the form of the

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gallium p orbital perpendicular to the coordination plane. This is similar to the Ga^I and In^I bis(phosphane) complexes[18] and lends the complex a germylene-like characterstic.

The C-Ga-C angle was calculated to be 100.0° with a Ga–C distance of 221 pm for the geometry-optimized $[Ga(TMI)_2]^+$ structure (Table 2) As in the experiment, the coordination is not in plane (pitch angles of 4.7°), although less pronounced than in the crystal structures. Steric reasons appear implausible here owing to the small ligand size. If, however, the mono(carbene) complex $[Ga(TMI)]^+$ is computed, a perfect pitch angle of 0° is found. To investigate whether orbital-based electronic effects are associated with the second coordination, one carbene ligand was substituted for a hydride ligand to mimic a σ donor without any back-bonding ability or steric demand. Surprisingly, a pitch angle of 12.4° was calculated for the optimized structure, accompanied by a strong decrease of the positive charge at gallium. Our working hypothesis is that Ga^+ (and In^+) are able to accommodate the electrons donated by one carbene ligand easily, but not those of a very electron-rich second ligand (compare with the charge distribution in Table 2). Back-bonding interactions are needed to distribute the electron density more evenly. A classical π-back-bonding interaction, as frequently discussed for transition-metal complexes, is not possible owing to the symmetry of the lone pair in the s orbital of the central metal. The tilting of the ligand allows the donation of electron density from the gallium s-type lone-pair orbital into the empty p orbital of the carbenes.[36] This effect may be compared to the somewhat similar interaction that causes the formation of the *trans*-bent-configured formal double bonds in the heavier disilenes, digermenes, and distannenes $R_2E{=}ER_2$ (see Figure 2).

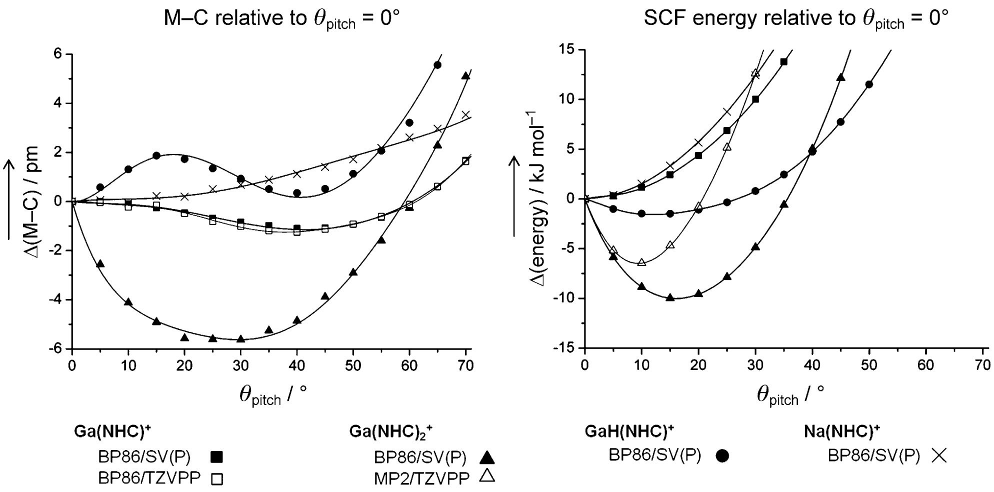

Figure 3. Coordination distance and energy profiles upon varying the pitch angles for $[Ga(NHC)]^+$, [GaH(NHC)], $[Ga(NHC)_2]^+$, and $[Na(NHC)]^+$ at the BP86/def-SV(P) level. All of the values are given relative to the straight coordination with a pitch angle of 0°. $\Delta(M{-}C) = M{-}C(\theta_{pitch}) - M{-}C(0°)$ and $\Delta(energy) = energy(\theta_{pitch}) - energy(0°)$.

If the hydride ligand is replaced by a carbonyl ligand, which is known to be a strong π-acceptor, the pitch angle decreases to 7.1° while the carbonyl shows an angle of 30.9° against the C–Ga axis. The increase in positive charge at gallium emphasizes the superior acceptor properties of the carbonyl ligand. Steric factors can again be ruled out. Bent Ga/In carbonyl complexes were previously proposed in low-temperature matrix studies and may arise for similar reasons.[37]

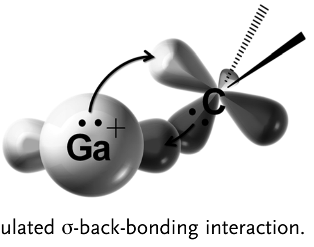

Figure 2. The postulated σ-back-bonding interaction.

This curious tilting was systematically further investigated by a series of geometry constrained structural optimizations. The pitch angles were varied in 5° steps starting from the planar position for $[Ga(NHC)]^+$, [GaH(NHC)], $[Ga(NHC)_2]^+$, and $[Na(NHC)]^+$. Sodium was included, as it forms complexes with similar coordination distances as Ga^+, but does not have the ability to back-bond. For reasons of computational simplicity and coordinate definitions in these restricted optimizations, the simplest NHC ($C_3N_2H_4$) with four H atoms instead of the CH_3 groups was used (Figure 3).

The mono(carbene) complex $Ga(NHC)^+$ shows the energy minimum at $\theta_{pitch} = 0°$, while the coordination distance interestingly has a minimum at 40°. The addition of the hydride ligand shifts the energy minimum to between 10 and 15° with two minima of the Ga–C distance at 0 and 40°. The bis(carbene) complex $[Ga(NHC)_2]^+$, however, shows minima for energy and d_{Ga-C} in the experimentally observed region (15° and 30°, respectively). The sodium complex $[Na(NHC)]^+$ has no lone pair available for back-donation, and thus shows a much simpler pattern with minima only at 0°. In summary, this indicates that back-bonding into p orbitals may indeed be the cause for the unique tilted carbene coordination mode. The scan along the pitch angle is also accompanied by a decrease of the occupation of the valence s orbital at gallium from 1.88 to a minimum of 1.81 at 35° (see the Supporting Information for a graphical representation of the population of s and p orbitals along the pitch angle scan).[38] At low angles up to the minimum angle of 35°, the population of the p orbitals increases concomitantly with the decrease of the

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s orbital population. This increase in p-population can only be attributed to standard σ donation from the carbenes into the p orbitals of gallium which are in plane with the ligands, as the population of the perpendicular p orbital remains almost constant and empty (0.02) at reasonable pitch angles. At higher angles, the p-orbital population decreases again as the s-population increases, and at angles close to 90° (and very long coordination distances) the electronic configuration of free Ga^+ is approached. This perfectly complements and supports the existence of the above described s-to-$p_{carbene}$ back donation. Such a σ-back-bonding interaction might well also occur in other related systems and might be a clue to the occasionally observed pitch and yaw angles in metal–carbene complexes.

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[1] J. B. Dumas, E. Peligot, *Ann. Chim. Phys.* **1835**, 5.
[2] K. Öfele, *J. Organomet. Chem.* **1968**, *12*, P42.
[3] H. W. Wanzlick, H. J. Schönherr, *Angew. Chem.* **1968**, *80*, 154; *Angew. Chem. Int. Ed. Engl.* **1968**, *7*, 141.
[4] A. J. Arduengo, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361.
[5] P. de Frémont, N. Marion, S. P. Nolan, *Coord. Chem. Rev.* **2009**, *253*, 862.
[6] G. C. Vougioukalakis, R. H. Grubbs, *Chem. Rev.* **2010**, *110*, 1746.
[7] W. A. Herrmann, *Angew. Chem.* **2002**, *114*, 1342; *Angew. Chem. Int. Ed.* **2002**, *41*, 1290.
[8] D. Bourissou, O. Guerret, F. P. Gabbaï, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39.
[9] D. Canella, S. J. Hock, O. Hiltner, E. Herdtweck, W. A. Herrmann, F. E. Kuhn, *Dalton Trans.* **2012**, *41*, 2110.
[10] X.-W. Li, J. Su, G. H. Robinson, *Chem. Commun.* **1996**, 2683.
[11] R. S. Ghadwal, H. W. Roesky, R. Herbst-Irmer, P. G. Jones, *Z. Anorg. Allg. Chem.* **2009**, *635*, 431.
[12] N. Kuhn, T. Kratz, D. Bläser, R. Boese, *Chem. Ber.* **1995**, *128*, 245.
[13] J. D. Gorden, C. L. B. Macdonald, A. H. Cowley, *J. Organomet. Chem.* **2002**, *643–644*, 487.
[14] C. D. Abernethy, M. L. Cole, C. Jones, *Organometallics* **2000**, *19*, 4852.
[15] S. J. Black, D. E. Hibbs, M. B. Hursthouse, C. Jones, K. M. Abdul Malik, N. A. Smithies, *J. Chem. Soc. Dalton Trans.* **1997**, 4313.
[16] R. J. Baker, H. Bettentrup, C. Jones, *Eur. J. Inorg. Chem.* **2003**, 2446.
[17] R. J. Baker, R. D. Farley, C. Jones, M. Kloth, D. M. Murphy, *Chem. Commun.* **2002**, 1196.
[18] A. Higelin, U. Sachs, S. Keller, I. Krossing, *Chem. Eur. J.* **2012**, *18*, 10029.
[19] J. M. Slattery, A. Higelin, T. Bayer, I. Krossing, *Angew. Chem.* **2010**, *122*, 3297; *Angew. Chem. Int. Ed.* **2010**, *49*, 3228.
[20] S. Welsch, M. Bodensteiner, M. Dušek, M. Sierka, M. Scheer, *Chem. Eur. J.* **2010**, *16*, 13041.
[21] A. Higelin, C. Haber, S. Meier, I. Krossing, *Dalton Trans.* **2012**, *41*, 12011.
[22] H. Jacobsen, A. Correa, A. Poater, C. Costabile, L. Cavallo, *Coord. Chem. Rev.* **2009**, *253*, 687.
[23] I. Krossing, *Chem. Eur. J.* **2001**, *7*, 490.
[24] A. J. Arduengo, R. Krafczyk, R. Schmutzler, H. A. Craig, J. R. Goerlich, W. J. Marshall, M. Unverzagt, *Tetrahedron* **1999**, *55*, 14523.
[25] M. R. Fructos, T. R. Belderrain, P. de Frémont, N. M. Scott, S. P. Nolan, M. M. Díaz-Requejo, P. J. Pérez, *Angew. Chem.* **2005**, *117*, 5418; *Angew. Chem. Int. Ed.* **2005**, *44*, 5284.
[26] P. de Frémont, N. M. Scott, E. D. Stevens, T. Ramnial, O. C. Lightbody, C. L. B. Macdonald, J. A. C. Clyburne, C. D. Abernethy, S. P. Nolan, *Organometallics* **2005**, *24*, 6301.
[27] Rapid relaxation caused by the interaction of the high quadrupolar moment of ^{71}Ga with the asymmetric coordination environment induced by carbene ligands, in contrast to the more uniform arene coordination, appears to render the detection of the ^{71}Ga nucleus impossible.
[28] O. Kühl, *Coord. Chem. Rev.* **2009**, *253*, 2481.
[29] W. A. Herrmann, F. C. Munck, G. R. J. Artus, O. Runte, R. Anwander, *Organometallics* **1997**, *16*, 682.
[30] A. J. Arduengo, R. Krafczyk, R. Schmutzler, W. Mahler, W. J. Marshall, *Z. Anorg. Allg. Chem.* **1999**, *625*, 1813.
[31] W. M. Boesveld, B. Gehrhus, P. B. Hitchcock, M. F. Lappert, P. von R. Schleyer, *Chem. Commun.* **1999**, 755.
[32] S. A. Mungur, S. T. Liddle, C. Wilson, M. J. Sarsfield, P. L. Arnold, *Chem. Commun.* **2004**, 2738.
[33] A. V. Protchenko, K. H. Birjkumar, D. Dange, A. D. Schwarz, D. Vidovic, C. Jones, N. Kaltsoyannis, P. Mountford, S. Aldridge, *J. Am. Chem. Soc.* **2012**, *134*, 6500.
[34] The brown solution showed the undisturbed signals of the anion, and no ^{71}Ga signal was observed. The ^1H NMR signals are observed in the range previously reported for $[Ag(IMes)_2]^+$[26] complexes (1.79 ppm for the *ortho*-methyl groups).
[35] D. J. D. Wilson, S. A. Couchman, J. L. Dutton, *Inorg. Chem.* **2012**, *51*, 7657.
[36] C. D. Abernethy, G. M. Codd, M. D. Spicer, M. K. Taylor, *J. Am. Chem. Soc.* **2003**, *125*, 1128.
[37] H.-J. Himmel, A. J. Downs, J. C. Green, T. M. Greene, *J. Phys. Chem. A* **2000**, *104*, 3642.
[38] A. E. Reed, R. B. Weinstock, F. Weinhold, *J. Chem. Phys.* **1985**, *83*, 735.

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