

See discussions, stats, and author profiles for this publication at:
<https://www.researchgate.net/publication/230556395>

Divalent carbon(o) compounds

ARTICLE · JANUARY 2009

CITATIONS

9

READS

17

2 AUTHORS, INCLUDING:



Ralf Tonner

Philipps University of Marburg

76 PUBLICATIONS 1,664 CITATIONS

SEE PROFILE

Divalent carbon(0) compounds*

Gernot Frenking^{1,†} and Ralf Tonner²

¹*Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Strasse, D-35032 Marburg, Germany;* ²*Centre for Theoretical Chemistry and Physics, New Zealand Institute for Advanced Study, Massey University Albany, Private Bag 102904, North Shore City, 0745 Auckland, New Zealand*

Abstract: Quantum chemical studies show that there is a class of carbon compounds with the general formula CL_2 where the carbon atom retains its four valence electrons as two lone pairs. The C–L bonds come from $L \rightarrow C$ donor–acceptor interactions where L is a strong σ -donor. Divalent C(0) compounds (carbones) are conceptually different from divalent C(II) compounds (carbenes) and tetravalent carbon compounds, but the bonding situation in a real molecule may be intermediate between the three archetypes. There are molecules like tetraaminoallenes which may be described in terms of two double bonds $(R_2N)_2C=C=C(NR_2)_2$ where the extraordinary donor strength of the dicoordinated carbon atom comes only to the fore through the interactions with protons and Lewis acids. They may be considered as “hidden divalent C(0) compounds”. The donor strength of divalent C(0) molecules has been investigated by calculations of the binding energies with protons and with main-group Lewis acids and the bond dissociation energies (BDEs) of transition-metal complexes.

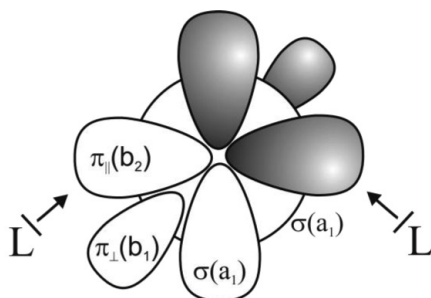
Keywords: bonding analysis; dicoordinated carbon; divalent C(0); carbenes; carbon compounds.

INTRODUCTION

The chemistry of organic compounds is mostly concerned with molecules where the tetravalent carbon atom uses all four valence electrons for chemical bonding which constitute single, double, or triple bonds in C(IV) compounds. Divalent C(II) compounds (carbenes) have played a prominent role in synthetic organic chemistry only since the ground-breaking works of Bertrand [1] and Arduengo [2]. Carbenes CR_2 have two electron-sharing bonds between carbon and the substituents R, and they possess one σ -type electron lone pair at C. Recent theoretical and experimental studies indicate that there is a promising but largely unknown class of organic compounds CL_2 where the carbon atom retains all four valence electrons in two lone-pair orbitals with σ and π symmetry, while the bonds $L \rightarrow C$ come from strong donor–acceptor interactions between a Lewis base L and the closed-shell carbon atom in the $(^1D) s^0 p_\sigma^2 p_{\pi\perp}^2 p_{\pi\parallel}^0$ configuration (Scheme 1) [3]. The latter species which have been termed “carbones” are divalent C(0) compounds because the carbon valence electrons are not directly involved in the C–L bonds [3–6].

*Paper based on a presentation at the 19th International Conference on Physical Organic Chemistry (ICPOC-19), 13–18 July 2008, Santiago de Compostela, Spain. Other presentations are published in this issue, pp. 571–776.

[†]Corresponding author



Scheme 1 Schematic representation of the bonding situation in divalent C(0) compounds CL_2 .

The first compound with the formula CL_2 which could become synthesized is the carbodiphosphorane (CDP) $\text{C}(\text{PPh}_3)_2$, which has been experimentally known since 1961 when it was synthesized by Ramirez et al. [7]. In the following years, CDPs became the subject of intense experimental studies and numerous compounds containing the CDP moiety could become isolated [8]. The bonding situation in CDP compounds was usually described in terms of double bonds $\text{R}_3\text{P}=\text{C}=\text{PR}_3$ or the bonding was compared with carbenes or ylides [8]. The description with two lone pairs at carbon has sometimes been used but it seems that the nature of the donor–acceptor bonding $\text{R}_3\text{P} \rightarrow \text{C} \leftarrow \text{PR}_3$ was not fully recognized [9]. A definite statement that CDPs should be considered as molecules which belong to the general class of divalent C(0) compounds CL_2 was made for the first time in the paper by Tonner et al. [4] who analyzed the electronic structure in $\text{C}(\text{PR}_3)_2$ for various groups R. In theoretical subsequent studies we investigated the structures and bonding situation in CL_2 compounds where $\text{L} = \text{PR}_3$, CO, and NHC (*N*-heterocyclic carbene) [3,5,6]. Because of the appearance of two lone-pair orbitals at the divalent C(0) atom, the compounds CL_2 are very strong Lewis bases which yield strongly bonded adducts with main-group Lewis acids and they are strongly bonded ligands in transition-metal complexes [6]. This was theoretically shown by calculating complexes where CL_2 compounds serve as electron donors. Divalent C(0) compounds are also very basic, which was shown by calculating their proton affinities [10]. The most important results about the divalent C(0) compounds and their complexes are summarized in this work.

METHODS

Geometry optimizations without symmetry constraints have been carried out using the Gaussian03 optimizer [11] together with TurboMole5 [12] energies and gradients at the BP86 [13]/def-SVP [14] (in the following, called SVP) level of theory. For the phenyl rings of PPh_3 -groups a minimal basis set has been used (benzene BS) except for the α -C atom. Stationary points were characterized as minima by calculating the Hessian matrix analytically [15]. Thermodynamic corrections and Kohn–Sham orbitals have been taken from these calculations. The standard state for all thermodynamic data is 298.15 K and 1 atm. The geometries of the parent compounds **1–6** have also been optimized at BP86/TZ2P with Amsterdam density functional (ADF) calculations [16]. Single-point energies at the BP86/def-SVP optimized geometries have been calculated with BP86 using the def2-TZVPP [17] basis set (in the following, called TZVPP). Uncontracted Slater-type orbitals (STOs) were employed as basis functions for the ADF calculations [18]. An auxiliary set of s, p, d, f, g, and h STOs was used to fit the molecular densities and to represent the Coulomb and exchange potentials accurately in each SCF cycle of the BP86/TZ2P calculations [19]. For the BP86/SVP and BP86/TZVPP calculations, the resolution-of-identity method has been applied [20]. The natural bond order (NBO) [21] analyses have been carried out with the internal module of Gaussian03 at the BP86/TZVPP level of theory.

PARENT COMPOUNDS CL₂

Figure 1 shows the optimized geometries of C(PPh₃)₂ (**1**), C(PPh₃)(CO) (**2**), C(CO)₂ (**3**), C(NHC_{Me})₂ (**4**), C[C(NMe₂)₂] (**5**), and the parent NHC (**6**). The latter compound was calculated for comparing divalent C(0) compounds (carbones) with an NHC. The calculated values are given at BP86/TZ2P and (in parentheses) at BP86/SVP. Experimental values are given in italics.

The calculated geometries at BP86/TZ2P are in very good agreement with the experiment. The BP86/SVP data also agree quite well with the measured data except for the bending angle α at the central carbon atom in **2**. The BP86/SVP calculations yield a nearly linear arrangement of the CO and PPh₃ ligands while the BP86/TZ2P calculations give a strongly bent geometry with $\alpha = 144.6^\circ$. The latter value is in very good agreement with the experimental data $\alpha = 145.6^\circ$ [41]. The theoretical results at BP86/TZ2P and the available experimental data given in Fig. 1 show that compounds **1**, **2**, and **4** are strongly bent while **3** and **5** are linear. Compound **3** is carbon suboxide [22], which is usually described with double bonds O=C=C=C=O, while compound **5** is named as tetrakisdimethylaminoallene [23]. The bending potentials of **1–5** are very shallow. Table 1 shows that the energy difference between the linear form and the bent structure with $\alpha = 136.9^\circ$, which is the optimized value for **1**, is very small. The largest value of 5.3 kcal/mol is calculated for the tetraaminoallene **5**, which is much smaller, however, than the calculated distortion energy for the parent allene H₂C=C=CH₂, which requires 16.3 kcal/mol (BP86/TZ2P) bending the molecule to a value of $\alpha = 136.9^\circ$.

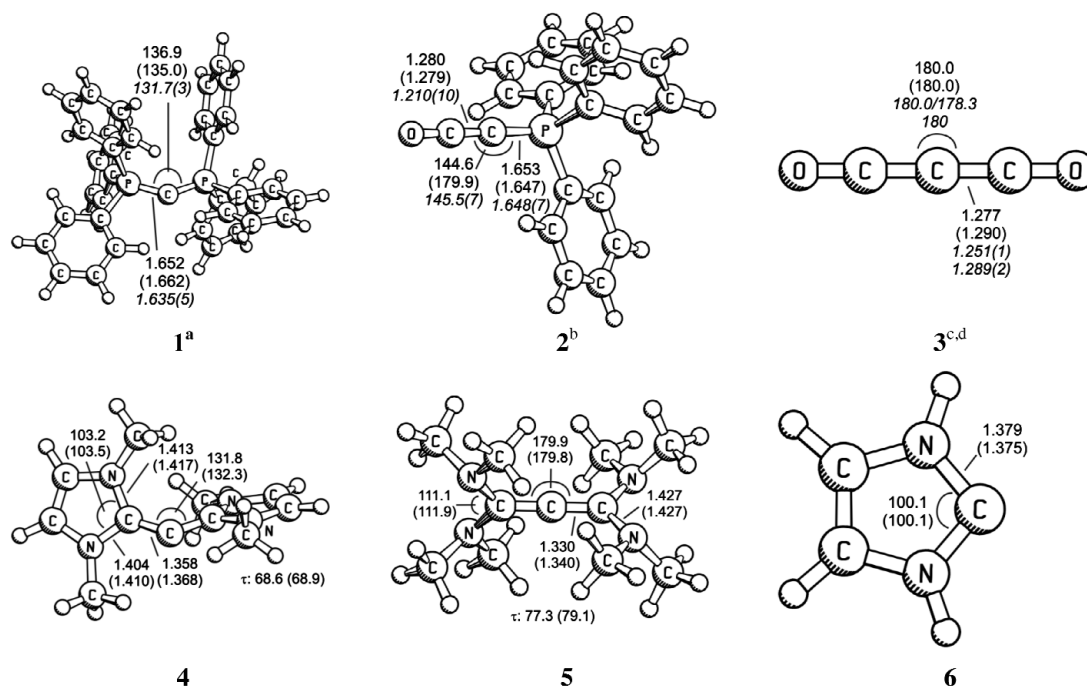
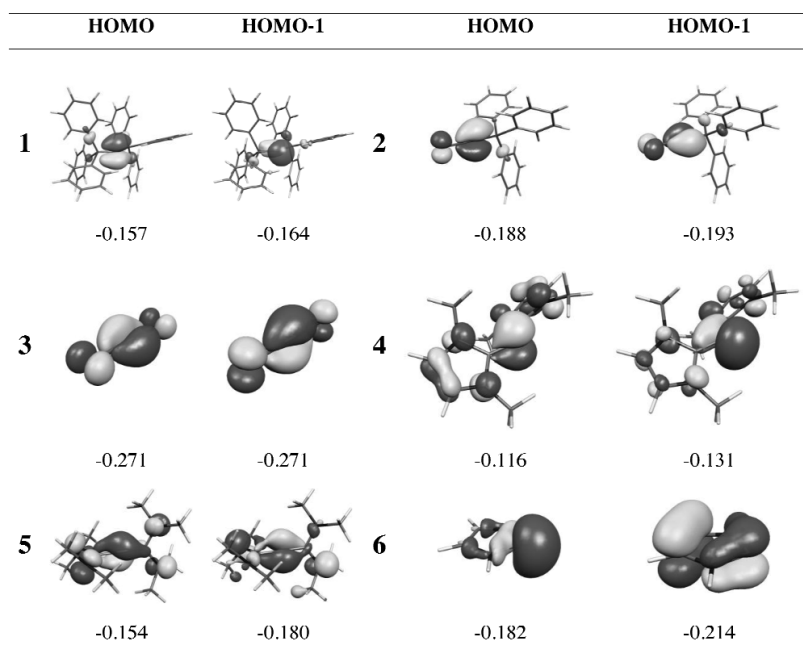


Fig. 1 Optimized geometries at BP86/TZ2P (BP86/SVP) of **1–6**. Experimental values are given in italics. Bond lengths in Å, angles in degree. ^aExperimental values from X-ray analysis taken from ref. [7b]. ^bExperimental values from X-ray analysis taken from ref. [41]. ^cExperimental values (top) from X-ray analysis taken from ref. [42]. ^dExperimental values (bottom) from electron diffraction taken from ref. [43].

Table 1 Calculated relative energies (BP86/TZ2P) of **1–5** with different bending angles α . All values in kcal/mol.

L_1	L_2	No.	Equilibrium structure	$\alpha = 180^\circ$	$\alpha = 136.9^\circ$
PPh_3	PPh_3	1	0.0	3.1	0.0
PPh_3	CO	2	0.0	0.3	0.5
CO	CO	3	0.0	0.0	1.9
NHC_{Me}	NHC_{Me}	4	0.0	3.2	0.1
$C(NMe_2)_2$	$C(NMe_2)_2$	5	0.0	0.0	5.3

Illuminating information about the bonding situation at the central carbon atom comes from the highest occupied molecular orbitals (HOMOs). Figure 2 shows the shape of the HOMO and the next lower-lying HOMO-1 of **1–6**. Visual inspection shows that the two highest-lying MOs of **1** are a π -type (HOMO) and σ -type (HOMO-1) lone-pair orbital at C. Substitution of one PPh_3 ligand by CO yields a Lewis structure for **2** which has delocalized π -type (HOMO) and σ -type (HOMO-1) orbitals. The HOMO and HOMO-1 of the linear structures of **3** and **5** are degenerate π -orbitals which are clearly delocalized over the ligands $L = CO$ and $L = (NMe_2)_2$. The carbodicarbene **4** has a π -type (HOMO) and σ -type (HOMO-1) lone-pair orbital at C, but they appear to be somewhat delocalized over the NHC ligands (Fig. 2). The HOMO of **6** is clearly a σ -type lone-pair orbital at C, but the π -type HOMO-1 is significantly delocalized over the NHC ring. The latter orbital belongs to the three occupied π -orbitals of **6** that are delocalized over the five-membered ring, which is an aromatic system [24]. We want to point out that the shape of the frontier orbitals of **1–5** nicely indicates the nature of the ligands L in the com-

**Fig. 2** Shape and eigenvalues (in eV) of the two highest-lying HOMOs and HOMO-1 of **1–6** at BP86/TZVPP/BP86/TZ2P.

pounds CL_2 . The PPh_3 ligand is essentially a σ -donor and thus, there is hardly any delocalization of the π -orbitals in $\text{C}(\text{PPh}_3)_2$ (**1**). The ligand NHC is often compared with phosphines, and both compounds are considered to be mainly σ -donor ligands [25]. It has been shown, however, that NHC does possess some π -acceptor strength in donor-acceptor complexes [26]. This is supported by the shape of the HOMO in $\text{C}(\text{NHC})_2$ (**4**) which shows some π -delocalization (Fig. 2). CO and $\text{C}(\text{NMe}_2)_2$ are good π -acceptor ligands which becomes obvious when the delocalized HOMO and HOMO-1 of $\text{C}(\text{CO})_2$ (**3**) and $\text{C}[\text{C}(\text{NMe}_2)_2]$ (**5**) are considered. The linear geometries of the latter species may thus be explained with the optimal overlap of the π -orbitals of the donor and acceptor moieties.

Table 2 gives the results of the NBO analysis of **1–6**. Figure 3 displays the most favorable Lewis structures, which are suggested by the NBO calculations. The atomic partial charges at the central carbon atom $q(\text{C})$ exhibit negative values for **1–5**. The dicoordinated carbon atom in $\text{C}(\text{PPh}_3)_2$ has a very large negative charge of $q(\text{C}) = -1.44$ which agrees with strong $\text{Ph}_3\text{P} \rightarrow \text{C}$ σ -donation and negligible π -backdonation. The negative charge at carbon decreases significantly when the Ph_3P ligand is substituted by CO with **1** (-1.44) > **2** (-0.96) > **3** (-0.55). It is interesting to note that the NHC ligands in **4** yield a negative charge of -0.51 , which is similar to the value in **3** where the central carbon atom is bonded to the π -acceptor ligand CO. The central carbon atom in the tetraaminoallene **5** carries a small negative charge of -0.22 while the carbene carbon atom in **6** has a slightly positive charge of 0.04 .

Inspection of the two-center localized orbitals, which are calculated by the NBO method shows that only **1** has two lone-pair orbitals at the central carbon atom (Table 2). The best Lewis structure of carbon suboxide (**2**) is degenerate, possessing alternating single and triple bonds $\text{O}^--\text{C}\equiv\text{C}-\text{C}\equiv\text{O}^+$ rather than double bonds, while **3** is calculated as $\text{Ph}_3\text{P}^+-\text{C}\equiv\text{C}-\text{O}^-$ (Figs. 3b and 3c). The NBO calculations of the carbodicarbene **4** and the tetraaminoallene **5** also do not give carbon lone-pair orbitals at the central carbon atoms (Table 2). Rather, a bonding situation similar to allenes with two double bonds $\text{C}=\text{C}=\text{C}$ is depicted (Figs. 3d and 3e). However, NBO calculations of **2–5** with enforced σ and π lone pairs at carbon give only slightly higher residual densities compared with the unconstrained calculation (Table 2) which points toward the “hidden double lone-pair character” of these compound. The NBO analysis of **6** gives a Lewis structure with a carbon σ -type lone-pair orbital (Fig. 3). The NBO calculation with enforcement of two carbon lone pairs gives a substantially larger residual density for **6** than the default calculation (Table 2). Note that the optimal Lewis structures for **1–6** given by the NBO method always possess an electron octet that is preferred over Lewis structures, which have the least formal charges.

Table 2 NBO results (BP86/TZVPP/BP86/TZ2P) for compounds **1–6**. Partial charges q and orbital populations are given in electrons.

L_1	L_2	No.	$q(\text{C}^a)$	$q(\text{E}^b)$	$\text{LP}(\text{C}^a)_\sigma$		$\text{LP}(\text{C}^a)_\pi$	Residual
					Occ ^d	%s ^d	Occ ^d	density ^{c,d}
PPh_3	PPh_3	1	-1.44	1.54	1.59	23.5%	1.52	3.1%
PPh_3	CO	2	-0.96	$1.55/0.58$	(1.40)	(3.7%)	(1.35)	3.2% (3.4%)
CO	CO	3	-0.55	0.65	(1.25)	(0.0%)	(1.25)	4.8% (4.9%)
NHC_{Me}	NHC_{Me}	4	-0.51	0.29	(1.46)	(5.8%)	(1.15)	2.3% (3.3%)
$\text{C}(\text{NMe}_2)_2$	$\text{C}(\text{NMe}_2)_2$	5	-0.22	0.25	(1.15)	(0.0%)	(1.10)	1.4% (2.9%)
	$\text{HN}=\text{CH}-\text{CH}=\text{NH}$	6	0.04	-0.53	1.91	51.5%	(0.67)	2.5% (5.1%)

^aCentral carbon atom.

^bAtom E which is directly bonded to the central carbon atom. For **1**: E = P; for **2**: E = P/C; for **3–5**: E = C; for **6**: E = N.

^cDensity that is left after the diagonalization step resulting in the NBOs. Given as total non-Lewis contribution in the NBO calculation.

^dValues in parentheses come from Lewis structures with two lone pairs at the central carbon atom, which have been enforced in the NBO calculations.

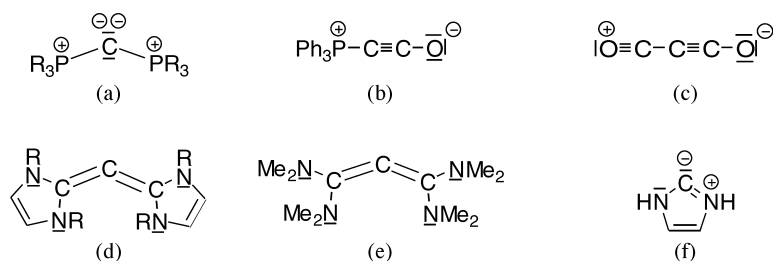


Fig. 3 Most favorable Lewis structures for **1–6** given by the NBO method. Only one of two equivalent Lewis structures is shown in c and f.

What does the analysis of the electronic structure suggest for the chemical behavior of **1–6**? In the next section we will discuss the theoretical results for the proton affinities and for donor–acceptor complexes of **1–6** with main-group Lewis acids BH_3 , CO_2 , and transition-metal complexes with **1–6** as ligands.

PROTON AFFINITIES AND DONOR–ACCEPTOR COMPLEXES OF **1–6**

The difference between divalent C(II) compounds (carbenes) and divalent C(0) compounds (carbenes) is, that the latter possess two electron lone pairs which are therefore capable of binding *two* monodentate Lewis acids and thus, they should be extremely strong Lewis bases. The experimentally observed chemical reactivity indicates that CDPs are indeed strong electron donors [27–31]. In order to estimate the donor strength of **1–6** we calculated the geometries and the bonding energies of complexes with one and with two Lewis acids H^+ , BH_3 , and CO_2 . The most important geometrical variables of $\text{L}_2\text{C}-\text{A}$ and $\text{L}_2\text{C}-\text{A}_2$ ($\text{A} = \text{H}^+$, BH_3 , and CO_2) are given in Table 3. Figure 4 shows the geometries of the complexes with BH_3 and CO_2 , which were found as equilibrium structures on the potential energy surfaces. Compounds **1–5** bind two BH_3 ligands in complexes $\text{L}_2\text{C}-(\text{BH}_3)_2$. The geometry optimizations of $\text{L}_2\text{C}-(\text{CO}_2)_2$ did not give minima for tetracoordinated carbon complexes except for **1**, which shows that the donor strength of the second electron lone pair of **2–4** is not large enough to bind two weak Lewis acids like CO_2 . **2** and **3** do not even bind one CO_2 molecule.

Figure 4 also gives experimental values for some compounds, which are available from the literature. The agreement between theory and experiment is generally quite good. Large differences come from substituent effects because some experimental data have been taken from substituted analogs. For a detailed discussion of the geometrical data we refer to our previous paper [6]. The most interesting aspect concerns the finding that even the carbon suboxide $\text{C}(\text{CO})_2$ and the tetraaminoallene $\text{C}[\text{C}(\text{NMe}_2)_2]$ which have a linear $\text{L}-\text{C}-\text{L}$ moiety bind two Lewis acids BH_3 although the parent system does not exhibit lone-pair orbitals at the central carbon atom. As noted before, it takes only a little energy to distort the linear form of **3** and **4** to a bent structure. Also, the NBO analysis indicates that the latter species possess “hidden divalent C(0) character” because the Lewis structure with two electron lone pairs at carbon is only slightly less favorable than the structure with double bonds.

Table 3 Calculated geometrical parameters of Lewis acid complexes **1-A** to **6-A** with **A** = **H⁺**, **BH₃**, **CO₂** at BP86/SVP. Distances in Å, bond angles in degrees. Experimental values from X-ray analyses are given in italics.

N	N-H⁺			N-BH₃			N-CO₂			N-(H⁺)₂			N-(BH₃)₂			N-(CO₂)₂		
	d(C-A)	d(C-L)	<(LCL)	d(C-A)	d(C-L)	<(LCL)	d(C-A)	d(C-L)	<(LCL)	d(C-A)	d(C-L)	<(LCL)	d(C-A)	d(C-L)	<(LCL)	d(C-A)	d(C-L)	<(LCL)
1	1.100	1.735	132.4	1.689	1.711	128.2	1.512	1.731/	137.0	1.110	1.869	131.0	1.730	1.810	119.2	1.564/	1.870/	123.6
		<i>1.722(4)^a</i>	<i>131.9(2)</i>				1.769				<i>1.816(4)^b</i>					1.657	1.899	
2	1.103	1.788/	123.3	1.713	1.736/	121.0		d		1.114	2.022/	115.8	1.805/	1.793/	117.0		d	
		1.337 ^c			1.324 ^c						1.407 ^c		1.763 ^c	1.356 ^c				
3	1.112	1.370	122.9	1.812	1.331	130.6		d		1.136	1.476	115.9	1.917	1.349	127.8		d	
4	1.099	1.418	126.1	1.665	1.413/	117.8	1.588	1.419	120.3	1.111	1.508	118.3	1.732	1.471	112.2		d	
		<i>1.413(4)^e</i>	<i>123.5(3)</i>		1.418													
5	1.099	1.422	129.1	1.654	1.417/	117.9	1.609	1.417	122.7	1.109	1.527	121.3	1.769	1.468	114.9		d	
		<i>1.375(4)^f</i>	<i>127.1(3)</i>		1.426						<i>1.511^f</i>	<i>112.5</i>						
6	1.096	1.345	106.9	1.587	1.364	103.3	1.556	1.345	106.4	1.124	1.450	101.1		g			d	
		<i>1.323(4)^h</i>	<i>108.4(2)</i>															
		<i>1.333(4)</i>																

^aRef. [45].

^bRef. [46].

^cTop entry is the C-PPh₃ bond length, bottom entry is the C-CO bond length.

^dDissociation occurs during optimization.

^eCO₂ deprotonates both NHCs.

^fRef. [34b].

^gOne BH₃ molecule dissociates and forms a B₂H₆-species with η¹-coordination toward the NHC.

^hRef. [48].

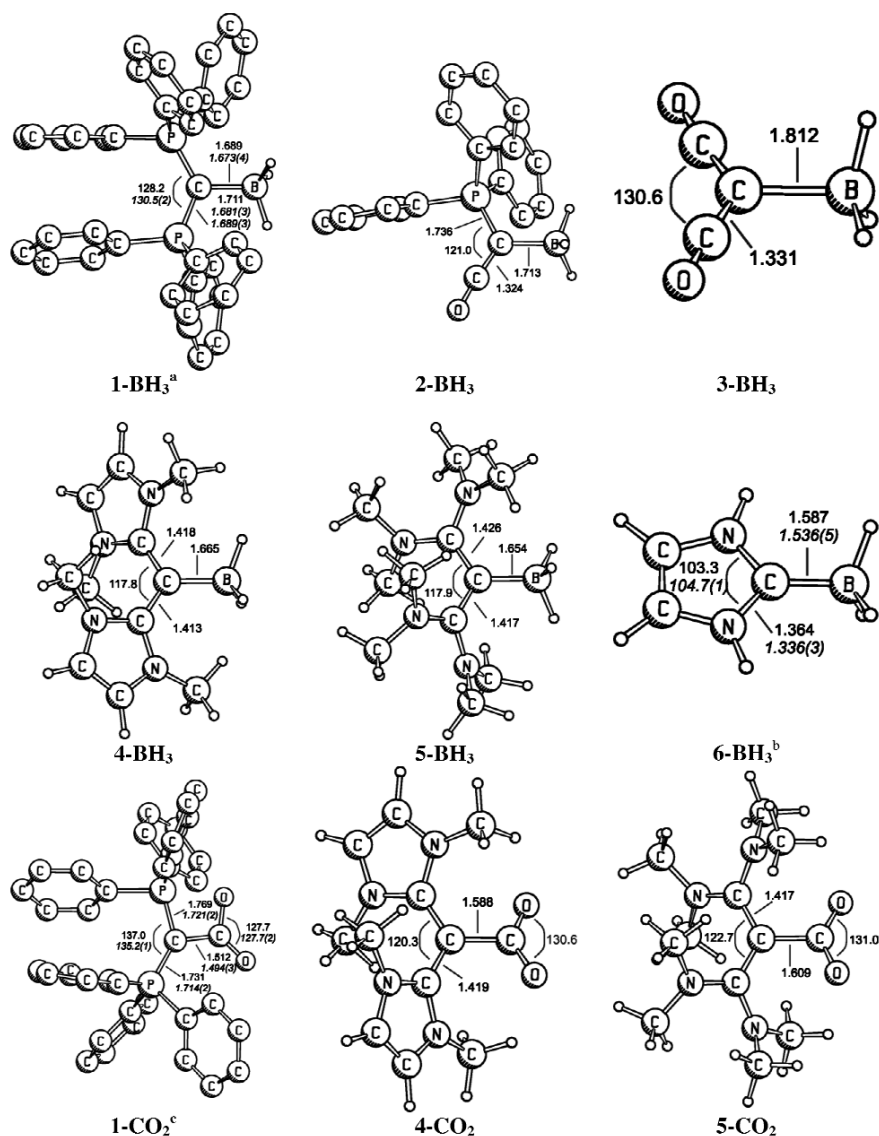


Fig. 4 Optimized geometries at BP86/SVP of N-BH₃, N-CO₂, N-(BH₃)₂, and N-(CO₂)₂ (N = 1–6) which were found as minima on the PES. Experimental values are given in italics. Bond lengths in Å, angles in degrees. Hydrogen atoms of the phenyl rings are omitted for clarity. ^aExperimental values from X-ray analysis taken from ref. [32]. ^bExperimental values from X-ray analysis of a substituted analog taken from ref. [35]. ^cExperimental values from X-ray analysis taken from ref. [29]. ^dExperimental values from X-ray analysis of a substituted analog taken from ref. [44].

(continues on next page)

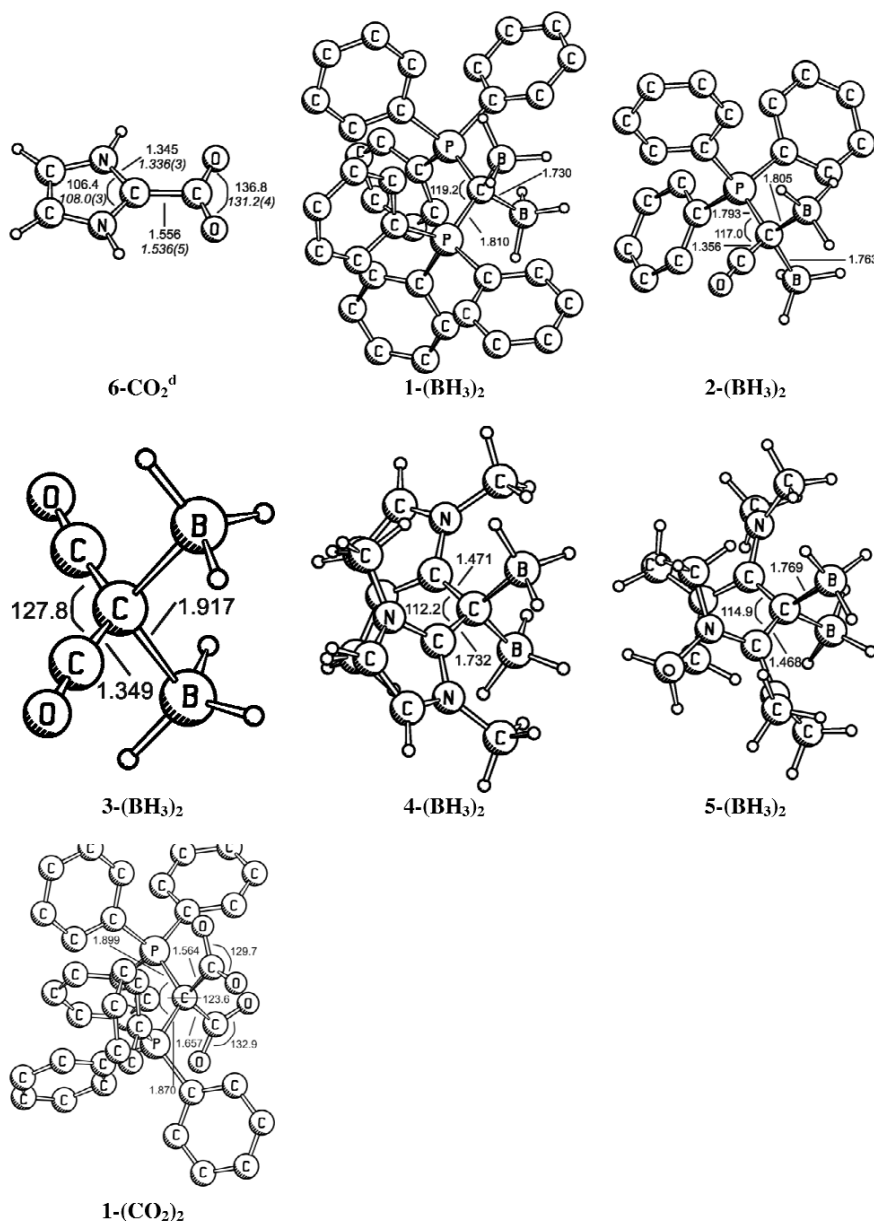


Fig. 4 (Continued).

Table 4 gives the calculated bond dissociation energies (BDEs) of the complexes L_2C-A and L_2C-A_2 ($A = H^+$, BH_3 , and CO_2). The calculated first protonation energies (PEs) of **1–6** are very large (>250 kcal/mol) except for **3**, which has a PE of only 181.8 kcal/mol. The theoretical values for the second PE give rather high values for **1**, **2**, **4**, and **5** (>125 kcal/mol) while the data for **3** (23.6 kcal/mol) and **6** (56.6 kcal/mol) are lower than for the other compounds. Note that the first and second protonation at the central carbon atom is always more favorable than protonation at a heteroatom! It is noteworthy that double protonation of the tetraaminoallene **5** preferentially takes place at a carbon atom for-

mally possessing two double bonds in the neutral form (Fig. 3) but not at the nitrogen atom [33]! The theoretical finding is supported by the X-ray analyses of derivatives of **5-H⁺** [34] and **5-(H⁺)₂** [34b].

Table 4 Dissociation energies (D_e) of Lewis acid complexes **1-A** to **6-A** and **1-A₂** to **6-A₂** with **A** = H⁺, BH₃, CO₂. Energies are given in kcal/mol at BP86 with the TZVPP basis set. BP86/SVP-geometries have been employed.

	N-H ⁺	N-BH ₃	N-CO ₂	N-(H ⁺) ₂	N-(BH ₃) ₂	N-(CO ₂) ₂
1	286.0	32.9	1.3	193.4	23.0	-16.3
2	252.5	28.7	a	129.7	11.7	a
3	181.6	10.0	a	23.6	2.3	a
4	297.5	46.1	13.2	170.3	24.3	a
5	292.2	37.2	4.3	158.5	9.5	a
6	259.9	58.6	10.4	56.6	c	a

^aDissociation occurs during optimization.

^bCO₂ deprotonates both NHCs.

^cOne BH₃ molecule dissociates and forms a B₂H₆-species with η¹-coordination toward the NHC.

The rather large bond energies for the BH₃ complexes (Table 4) suggest that all complexes L₂C-BH₃ should be synthetically accessible although **3-BH₃** has a comparatively weak bond. Note that the complex **1-CO₂**, which has a calculated BDE of only 1.3 kcal/mol, has been isolated and could become structurally characterized by X-ray analysis [29]. Since intermolecular interactions may contribute to the stability of molecules in the condensed phase it is possible to isolate even weakly bonded species. The complexes **1-BH₃** [32] and a substituted analog of **6-BH₃** that possesses ethyl substituents at the nitrogen atoms and methyl groups in the 4- and 5-positions of the imidazol-2-ylidene ring [35] are already known but the bond strength has not been measured. The calculated bond energies for the second BH₃ ligand of the complexes **1-(BH₃)₂** and **4-(BH₃)₂** are still quite high, while the BDE values for **2-(BH₃)₂**, **5-(BH₃)₂**, and particularly **3-(BH₃)₂** are rather small. It is remarkable that the latter species is a minimum on the potential energy surface.

The geometry optimization of **6-(BH₃)₂** leads to a structure where the second boron atom binds via a B-H-B bridge to the first BH₃ molecule and looses contact to the NHC ring. Experimental studies aiming at isolating **1-(BH₃)₂** resulted in isolation of an ionic complex [(μ-H)H₄B₂]C(PPh₃)₂(B₂H₇). The X-ray analysis showed that the complex has two boron-carbon donor-acceptor bonds between the C(PPh₃)₂ donor species and the [B₂H₅]⁺ acceptor moiety, which has a B-H-B bridge [32].

The weaker Lewis acid CO₂ yields complexes L₂C-CO₂ only for L₂C = **1**, **4**, and **5**, which have lower BDEs than L₂C-BH₃ (Table 4). Attempts to optimize the geometries of **2-CO₂** and **3-CO₂** showed that CO₂ dissociates during the optimization. As mentioned above, the complex **1-CO₂** has been isolated in the solid state [29] although the calculations give a BDE of only 1.3 kcal/mol. The isolation of the tetraaminoallene adduct **5-CO₂** has been reported with ethyl groups at nitrogen instead of methyl but the structure has not been determined [23]. The calculations predict (Table 4) that the BDE is only 4.3 kcal/mol. The NHC complex **6-CO₂** has been isolated as well [44]. Thus, it is conceivable that **4-CO₂** (D_e = 13.2 kcal/mol) might become isolated because the calculated BDE is clearly higher than for **1-CO₂** and **5-CO₂**. The only energy minimum structure of a complex with CO₂ ligands could become optimized for **1-(CO₂)₂**. However, the calculations predict that the latter species is unstable toward loss of the second CO₂ ligand and thus, it is unlikely that it will be experimentally observed.

The calculated BDEs suggest that the second PE is a useful probe in order to find out if a dicoordinated carbon molecule should be classified as divalent C(0) compound. According to the data shown in Table 4 it becomes obvious that **1**, **2**, **4**, and **5** should be considered as divalent C(0) species. The equilibrium geometry and the bonding analysis of **5** suggest that it is a tetraaminoallene. The calculated strong donor property of **5**, which is supported by experimental observations [34,36], indicates that the molecule may be considered as “hidden divalent C(0) species”.

The interpretation of the compounds L_2C in terms of $L \rightarrow C$ donor interactions is very helpful when the atomic partial charges of the complexes L_2C-A and L_2C-A_2 ($A = H^+$, BH_3 , and CO_2) are compared with the values for the parent compounds **1–6**. The calculated data are given in Table 5. Protonation of **1** and **2** reduces the negative charge at the central carbon atom by only a small amount. Surprisingly, the central carbon atom in **3-H⁺**, **4-H⁺**, and **5-H⁺** carries a higher negative charge than in the neutral compound. This is particularly striking for the tetraaminoallene **5** where the negative charge in the neutral compound (-0.21 e) increases to -0.47 e in the C-protonated species **5-H⁺**. The counter-intuitive increase of negative charge of an atom after protonation reveals that the “hidden” divalent C(0) character of **5** comes to the fore through protonation at the carbon atom. The higher negative charge at the central carbon atom of **3-H⁺**, **4-H⁺**, and **5-H⁺** can be explained with the enhanced charge donation $L_2C \rightarrow C(H^+) \leftarrow CL_2$ that compensates for the charge flow to the proton ($L_2C)C \rightarrow H^+$. A similar observation can be made for the other complexes L_2C-BH_3 and L_2C-CO_2 where the negative charge at the carbon donor atom decreases only a little or it becomes even larger like in **3-BH₃**, **5-BH₃**, and **5-CO₂**. The carbene donor atom in protonated NHC **6-H⁺** and in the complexes **6-BH₃** and **6-CO₂** behaves clearly differently because it is the only donor atom remaining positively charged.

Surprising features are also found when the calculated partial charges in the doubly protonated species **N-(H⁺)₂** ($N = 1-6$) and in **N-(BH₃)₂** ($N = 1-5$) are examined (Table 5). All tetracoordinated carbon donor atoms carry a negative partial charge even in the dications! The second protonation yields only slightly less negatively charged carbon donor atoms in **1-(H⁺)₂** and **2-(H⁺)₂** compared with the monocations but the carbon donor atoms in the dications **3-(H⁺)₂**–**5-(H⁺)₂** are more negatively charged than in the respective monocations. The change in the partial charge from cation to dication is particularly striking for the doubly protonated NHC **6-(H⁺)₂** where the second protonation turns the positively charged carbon atom into a negatively charged species. The change of the atomic partial charges at the carbon atom after complexation by H^+ , BH_3 , or CO_2 turns chemical intuition upside down. The truly bewildering partial charges can be understood in the light of the donor–acceptor bonding situation of divalent C(0) compounds.

Table 5 NBO partial charges (BP86/TZVPP/BP86/SVP) for parent compounds **N** and the complexes **N-H⁺**, **N-BH₃**, **N-CO₂**, **N-(H⁺)₂**, **N-(BH₃)₂**, and **N-(CO₂)₂** (**N** = **1-6**). Atomic partial charges (in e) are given for the central carbon atom [*q*(C)] and the whole CL₂-fragment [*q*(CL₂)].

$$\begin{array}{c} \text{L}_1 \backslash \text{C}-\text{A} \\ \text{L}_2 \end{array}$$

$$\begin{array}{c} \text{L}_1 \backslash \text{C} \backslash \text{A} \\ \text{L}_2 \end{array}$$

	N		N-H⁺		N-BH₃		N-CO₂		N-(H⁺)₂		N-(BH₃)₂		N-(CO₂)₂	
	L ₁	L ₂	<i>q</i> (C)	<i>q</i> (C)	<i>q</i> (CL ₂)	<i>q</i> (C)	<i>q</i> (CL ₂)	<i>q</i> (C)	<i>q</i> (CL ₂)	<i>q</i> (C)	<i>q</i> (CL ₂)	<i>q</i> (C)	<i>q</i> (CL ₂)	<i>q</i> (CL ₂)
1	PPh ₃	PPh ₃	-1.43	-1.33	+0.70	-1.30	+0.48	-1.14	+0.61	-1.07	+1.41	-1.11	-0.89	+1.14
2	PPh ₃	CO	-0.96	-0.91	+0.68	-0.86	+0.45		^a	-0.88	+1.29	-0.84	+0.72	^a
3	CO	CO	-0.55	-0.67	+0.62	-0.56	+0.31		^a	-0.74	+1.10	-0.60	+0.47	^a
4	NHC ^{Me}	NHC ^{Me}	-0.50	-0.52	+0.75	-0.40	+0.55	-0.42	+0.70	-0.53	+1.42	-0.50	+0.92	^a
5	C(NMe ₂) ₂	C(NMe ₂) ₂	-0.21	-0.47	+0.76	-0.36	+0.55	-0.37	+0.70	-0.51	+1.51	-0.49	+0.84	^a
6	HN=CH-CH=NH		0.04	+0.20	+0.73	+0.32	+0.50	+0.30	+0.64	-0.14	+1.29	^b	0.00	^a

^aDissociation occurs during optimization.

^bOne BH₃ molecule dissociates and forms a B₂H₆-species with η¹-coordination toward the NHC moiety.

The donor properties of **1–6** have also been probed in transition-metal complexes N-W(CO)_5 , N-Ni(CO)_3 , and N-Ni(CO)_2 ($\text{N} = \mathbf{1-6}$). Figure 5 shows the optimized geometries at BP86/SVP and the calculated BDEs of the $\text{L}_2\text{C-M(CO)}_n$ bonds at BP86/TZVPP//BP86/SVP. Figure 5 also gives the experimental bond lengths and bond angles for **1-Ni(CO)**₃ [29] and **1-Ni(CO)**₂ [29] and for substituted analogs of **6-W(CO)**₅ [36], **6-Ni(CO)**₃ [37], and **6-Ni(CO)**₂ [37]. The agreement between theory and experiment is very good. The optimized geometry of **6-Ni(CO)**₂ has a NHC ligand which is orthogonal to the plane of the Ni(CO)_2 moiety (C_{2v} symmetry) which agrees with the X-ray structure analysis of an N-substituted homolog [37]. The calculated data for the other compounds may thus serve as a reliable prediction for future measurements. The calculated C–Ni bonds in the 18-electron complexes N-Ni(CO)_3 are always longer than in the complexes N-Ni(CO)_2 which are formally 16-electron complexes if the ligands **N** are considered as two-electron donors. It will be interesting to see if the CL_2 ligands use both electron lone pairs for the C–Ni bonds in the latter species, which would explain the shorter and stronger bonds. Note that the C_3O_2 ligand changes its coordination mode from η^1 in **3-Ni(CO)**₃ to η^2 in **3-Ni(CO)**₂.

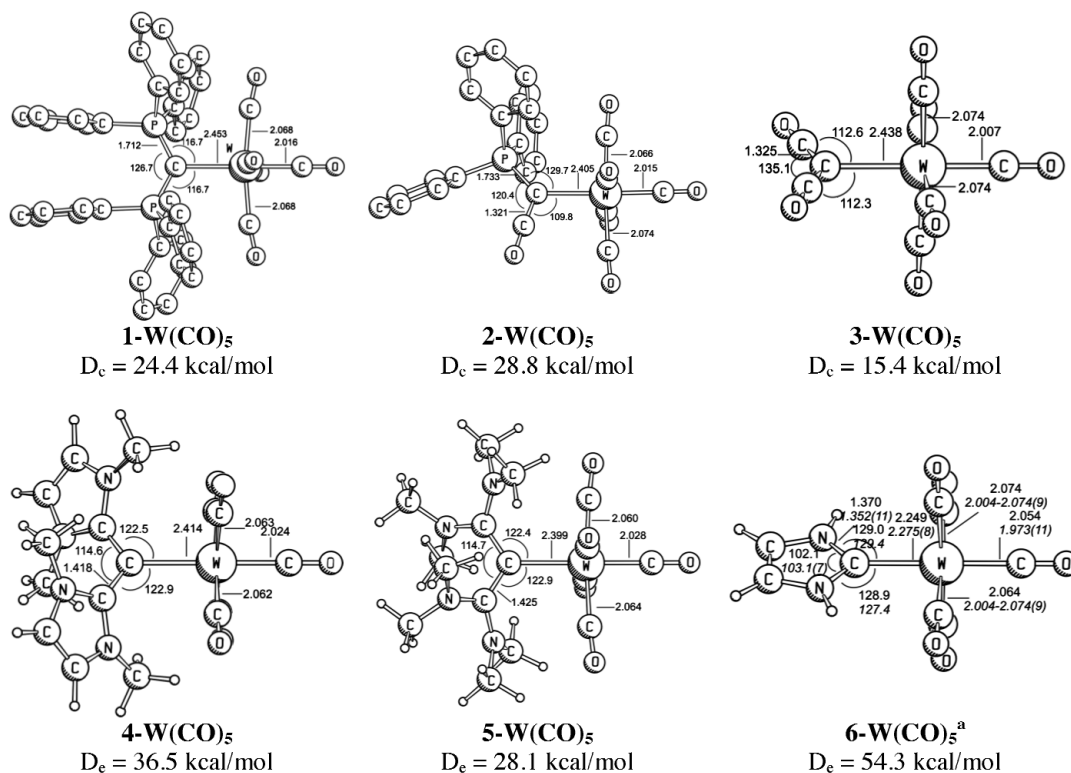


Fig. 5 Optimized geometries at BP86/SVP of N-W(CO)_5 , N-Ni(CO)_3 and N-Ni(CO)_2 ($\text{N} = \mathbf{1-6}$) which were found as minima on the PES. Experimental values are given in italics. Bond lengths in Å, angles in degree. Hydrogen atoms of the phenyl rings are omitted for clarity. ^aExperimental values from X-ray analysis taken from ref. [36]. ^bExperimental values from X-ray analysis taken from ref. [31]. ^cExperimental values from X-ray analysis of a substituted analog taken from ref. [37]. ^dExperimental values from X-ray analysis taken from ref. [31]. ^eExperimental values from X-ray analysis of a substituted analog taken from ref. [37]. BDEs (D_c) for the N–M bond are given at the BP86/TZVPP//BP86/SVP level of theory.

(continues on next page)

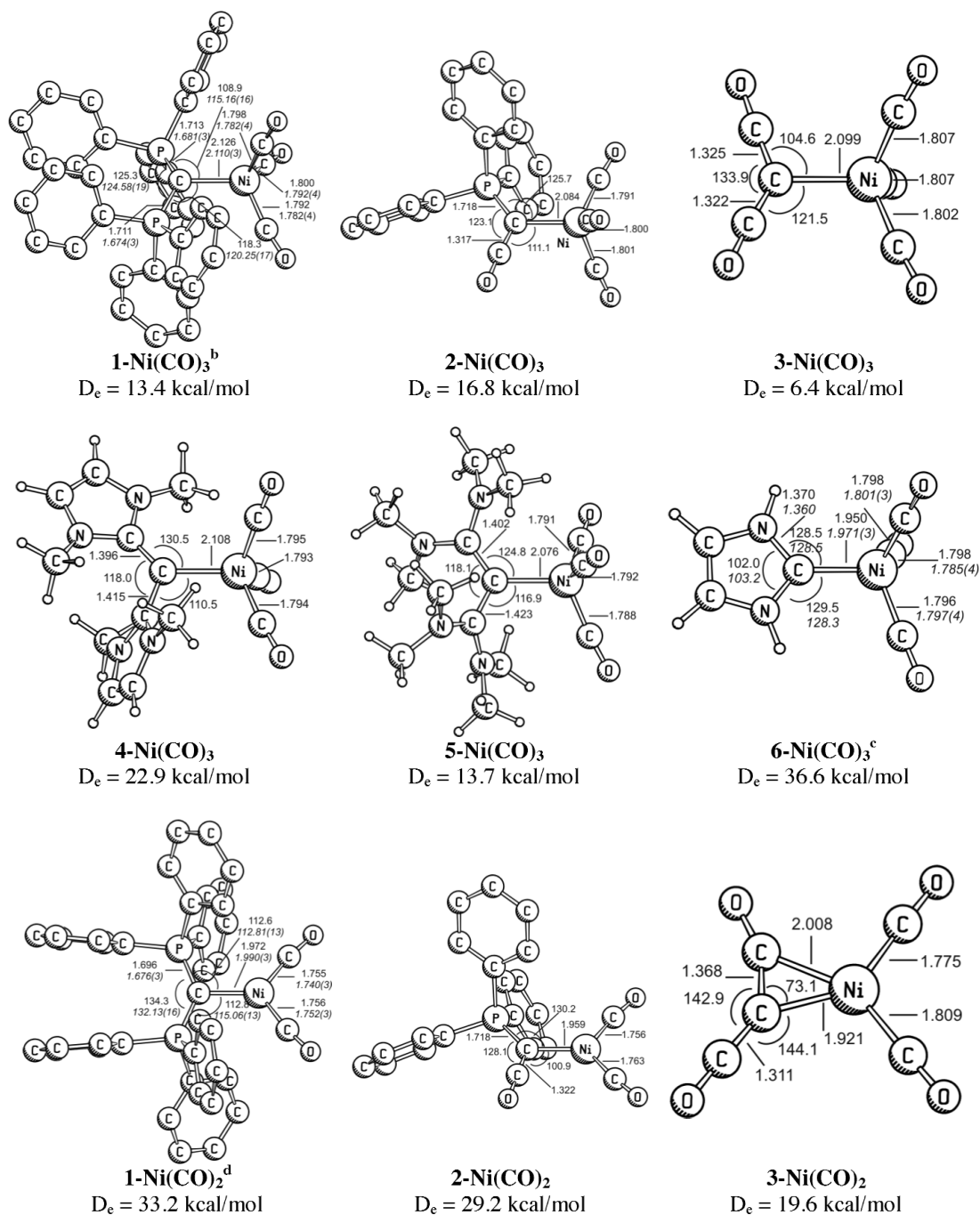


Fig. 5 (Continued).

(continues on next page)

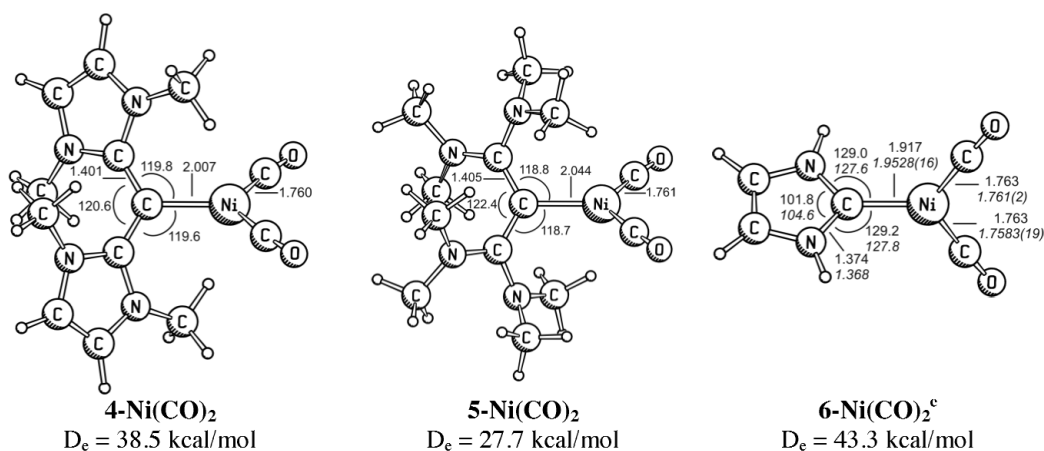


Fig. 5 (Continued).

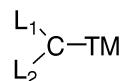
The calculated BDE values indicate (Fig. 5) that the L_2C-W bonds in $N-W(CO)_5$ have a similar strength as the L_2C-B bonds in $N-BH_3$ (Table 4). The strongest bond is predicted for **6-W(CO)₅** ($D_e = 54.3$ kcal/mol) while the weakest bond is calculated for **3-W(CO)₅** ($D_e = 15.4$ kcal/mol). The BDE values for $N-W(CO)_5$ shall be compared with the calculated result for $W(CO)_6$ ($D_e = 44.5$ kcal/mol) obtained at the same level of theory. The latter value gives a theoretical BDE of $D_0^{298} = 43.0$ kcal/mol after correction for thermal and ZPE contributions, which is in excellent agreement with the experimental value of 46 ± 2 kcal/mol [38]. The data suggest that the carbene **6** yields a stronger bond with $W(CO)_5$ than CO, while the other carbon donor ligands have weaker bonds. It is noteworthy that the synthesis of **1-W(CO)₅** was reported more than 30 years ago by Kaska et al. [9], but attempts to obtain crystals which are suitable for X-ray diffraction analysis were unsuccessful [39]. The calculated BDE for **1-W(CO)₅** ($D_e = 24.4$ kcal/mol), which is a lower bound, should be sufficient to isolate the compound. The very high basicity of the divalent C(0) compounds easily leads to side reactions particularly in protic solvents, but the development of experimental methods in the last three decades should eventually lead to the isolation of complexes $N-W(CO)_5$ ($N = 1-6$). The synthesis of **3-W(CO)₅** would realize a new binding mode of carbon suboxide, which has not been observed so far [40].

The calculated BDE values for $N-Ni(CO)_3$ and $N-Ni(CO)_2$ suggest that the L_2C-Ni bonds are weaker than the respective L_2C-W bonds and that the $L_2C-Ni(CO)_2$ bonds are always stronger than the particular $L_2C-Ni(CO)_3$ bond (Fig. 5). The theoretically predicted trend of the bond energies is $L_2C-W(CO)_5 > L_2C-Ni(CO)_2 > L_2C-Ni(CO)_3$. The calculated bond energies for **6-Ni(CO)₃** and **6-Ni(CO)₂** can be compared with experimentally estimated values for N-substituted analogs that were recently published by Nolan et al. [37]. The bond strength of the $NHC_{Ad}-Ni(CO)_2$ - and $NHC_{t-Bu}-Ni(CO)_2$ complexes (Ad = adamantyl; *t*-Bu = *tert*-butyl) was given as 42 and 37 kcal/mol, respectively. This is in very good agreement with the theoretical BDE for the parent system **6-Ni(CO)₂**, which is estimated after considering thermal and entropic contributions as $D_0^{298} = 41.7$ kcal/mol. The theoretical value for **6-Ni(CO)₃** of $D_0^{298} = 34.7$ kcal/mol is somewhat larger than the experimental estimate $NHC_{Mes}-Ni(CO)_3 \geq 24$ kcal/mol $\geq NHC_{Ad}-Ni(CO)_3$ (Mes = mesityl) [37] but the difference may partly be caused by the bulky substituents.

The atomic partial charges for the transition-metal complexes $N-W(CO)_5$, $N-Ni(CO)_3$, and $N-Ni(CO)_2$ are given in Table 6. The data indicate that the carbon donor atom retains its negative partial charge in $1-TM(CO)_n - 6-TM(CO)_n$ which becomes even slightly more negative in the complexes compared with the free ligands (Table 5). This can be explained with the enhanced charge donation $L_2 \rightarrow C$ that compensates for the $L_2C \rightarrow M(CO)_n$ donation. The overall partial charges of the CL_2 lig-

ands have positive values except for the C_3O_2 ligand in **3-Ni(CO)₃** and **3-Ni(CO)₂** and the mixed $Ph_3P-C-CO$ ligand in **2-Ni(CO)₂** (Table 6). The negative value for $q(CL_2)$ is caused by $L_2C \leftarrow TM$ π -backdonation when $L = CO$. Please note that the tungsten atom in the complexes always carries a significant negative charge while the nickel atom is always positively charged in $N-Ni(CO)_n$.

Table 6 NBO results (BP86/TZVPP//BP86/SVP) for **N-W(CO)₅**, **N-Ni(CO)₃**, **N-Ni(CO)₂** ($N = 1-6$). Atomic partial charges (in e) are given for the central carbon atom [$q(C)$], the metal atom [$q(M)$] and the whole CL_2 -fragment [$q(CL_2)$].



	L_1	L_2	$W(CO)_5$			TM $Ni(CO)_3$			$Ni(CO)_2$		
			$q(C)$	$q(CL_2)$	$q(M)$	$q(C)$	$q(CL_2)$	$q(M)$	$q(C)$	$q(CL_2)$	$q(M)$
1-TM	PPh_3	PPh_3	-1.41	+0.27	-0.59	-1.47	+0.08	+0.46	-1.55	+0.03	+0.35
2-TM	PPh_3	CO	-0.95	+0.24	-0.63	-1.04	+0.07	+0.41	-1.09	-0.01	+0.35
3-TM	CO	CO	-0.64	+0.12	-0.64	-0.68	-0.10	+0.31	-0.68	-0.32	+0.39
4-TM	NHC_{Me}	NHC_{Me}	-0.53	+0.37	-0.62	-0.59	+0.17	+0.43	-0.64	+0.15	+0.29
5-TM	$C(NMe_2)_2$	$C(NMe_2)_2$	-0.45	+0.38	-0.61	-0.53	+0.19	+0.44	-0.57	+0.13	+0.31
6-TM	$HN=CH-CH=NH$		+0.19	+0.32	-0.72	0.04	+0.13	+0.41	+0.01	+0.13	+0.27

SUMMARY

The theoretical results of this work clearly show that there is a class of carbon compounds with the general formula CL_2 where the carbon atom retains its valence electrons as two lone pairs. The $C-L$ bonds come from $L \rightarrow C$ donor-acceptor interactions where L is a strong σ -donor. Divalent $C(0)$ compounds (carbenes) are conceptually different from divalent $C(II)$ compounds (carbenes) and tetravalent carbon compounds but the bonding situation in a real molecule may be intermediate between the three archetypes. There are molecules like tetraaminoallenes which may be described in terms of two double bonds $(R_2N)_2C=C=C(NR_2)_2$ where the extraordinary donor strength of the dicoordinated carbon atom comes only to the fore through the interactions with protons and Lewis acids. They may be considered as "hidden divalent $C(0)$ compounds". The donor strength of divalent $C(0)$ molecules should be further explored in synthesizing donor-acceptor complexes, which might possess interesting chemical properties.

ACKNOWLEDGMENTS

This work was supported by the Deutsche Forschungsgemeinschaft. RT thanks the German Academic Exchange Service (DAAD) for support via a postdoctoral fellowship. Excellent service by the Hochschulrechenzentrum of the Philipps-Universität Marburg is gratefully acknowledged. Further computer time was provided by the CSC Frankfurt, HLRS Stuttgart, and HHLRZ Darmstadt.

REFERENCES AND NOTES

- (a) A. Baceiredo, G. Bertrand, G. Sicard. *J. Am. Chem. Soc.* **107**, 4781 (1985); (b) A. Igau, H. Grützmacher, A. Baceiredo, G. Bertrand. *J. Am. Chem. Soc.* **110**, 6463 (1988); (c) A. Igau, A. Baceiredo, G. Trinquier, G. Bertrand. *Angew. Chem.* **101**, 617 (1989); (d) A. Igau, A. Baceiredo, G. Trinquier, G. Bertrand. *Angew. Chem., Int. Ed.* **28**, 621 (1989).
- A. J. Arduengo III, R. L. Harlow, M. Kline. *J. Am. Chem. Soc.* **113**, 2801 (1991).

3. R. Tonner, G. Frenking. *Chem.—Eur. J.* **14**, 3260 (2008).
4. (a) R. Tonner, F. Öxler, B. Neumüller, W. Petz, G. Frenking. *Angew. Chem.* **118**, 8206 (2006); (b) R. Tonner, F. Öxler, B. Neumüller, W. Petz, G. Frenking. *Angew. Chem., Int. Ed.* **45**, 8038 (2006).
5. (a) R. Tonner, G. Frenking. *Angew. Chem.* **119**, 8850 (2007); (b) R. Tonner, G. Frenking. *Angew. Chem., Int. Ed.* **46**, 8695 (2007).
6. R. Tonner, G. Frenking. *Chem.—Eur. J.* **14**, 3273 (2008).
7. (a) F. Ramirez, N. B. Desai, B. Hansen, N. McKelvie. *J. Am. Chem. Soc.* **83**, 3539 (1961); (b) G. E. Hardy, J. I. Zink, W. C. Kaska, J. C. Baldwin. *J. Am. Chem. Soc.* **100**, 8002 (1978).
8. Recent reviews: (a) N. D. Jones, R. G. Cavell, *J. Organomet. Chem.* **690**, 5485 (2005); (b) O. I. Kolodiaznyi. *Phosphorous Ylides: Chemistry and Application in Organic Synthesis*, Wiley-VCH, Weinheim (1999); (c) O. I. Kolodiaznyi. *Tetrahedron* **52**, 1855 (1996); (d) A. W. Johnson (Ed.). *Ylides and Imines of Phosphorus*, John Wiley, New York (1993).
9. W. C. Kaska, D. K. Mitchell, R. F. Reichelderfer. *J. Organomet. Chem.* **47**, 391 (1973).
10. R. Tonner, G. Heydenrych, G. Frenking. *ChemPhysChem* **9**, 1474 (2008).
11. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople. Gaussian 03, Revision C.02, Gaussian, Inc., Wallingford, CT (2004).
12. R. Ahlrichs, M. Baer, M. Haeser, H. Horn, C. Koelmel. *Chem. Phys. Lett.* **162**, 165 (1989).
13. (a) A. D. Becke. *Phys. Rev. A* **38**, 3098 (1988); (b) J. P. Perdew. *Phys. Rev. B* **33**, 8822 (1986).
14. A. Schaefer, H. Horn, R. Ahlrichs. *J. Chem. Phys.* **97**, 2571 (1992).
15. P. Deglmann, F. Furche, R. Ahlrichs. *Chem. Phys. Lett.* **362**, 511 (2002).
16. (a) F. M. Bickelhaupt, E. J. Baerends. In *Reviews In Computational Chemistry*, Vol. 15, p. 1, Wiley-VCH, New York (2000); (b) G. Te Velde; F. M. Bickelhaupt, E. J. Baerends, C. Fonseca Guerra, S. J. A. Van Gisbergen, J. G. Snijders, T. Ziegler. *J. Comput. Chem.* **22**, 931 (2001).
17. F. Weigend, R. Ahlrichs. *Phys. Chem. Chem. Phys.* **7**, 3297 (2005).
18. J. G. Snijders, E. J. Baerends, P. Vernooijs. *At. Nucl. Data Tables* **26**, 483 (1982).
19. J. Krijn, E. J. Baerends. *Fit Functions in the HFS-Method*, Internal Report (in Dutch), Vrije Universiteit Amsterdam, The Netherlands (1984).
20. (a) K. Eichkorn, O. Treutler, H. Ohm, M. Häser, R. Ahlrichs. *Chem. Phys. Lett.* **242**, 652 (1995); (b) F. Weigend. *Phys. Chem. Chem. Phys.* **8**, 1057 (2006).
21. A. E. Reed, L. A. Curtiss, F. Weinhold. *Chem. Rev.* **88**, 899 (1988).
22. (a) O. Diels, B. Wolf. *Ber. Dtsch. Chem. Ges.* **39**, 689 (1906); (b) H. G. Viehe, Z. Janousek, R. Gompper, D. Lach. *Angew. Chem., Int. Ed. Engl.* **12**, 566 (1973).
23. (a) H. G. Viehe, Z. Janousek, R. Gompper, D. Lach. *Angew. Chem.* **85**, 581 (1973); (b) H. G. Viehe, Z. Janousek, R. Gompper, D. Lach. *Angew. Chem., Int. Ed. Engl.* **12**, 566 (1973).
24. C. Boehme, G. Frenking. *J. Am. Chem. Soc.* **118**, 2039 (1996).

25. (a) T. Weskamp, F. J. Kohl, W. Hieringer, D. Gleich, W. A. Herrmann. *Angew. Chem.* **111**, 2573 (1999); (b) T. Weskamp, F. J. Kohl, W. Hieringer, D. Gleich, W. A. Herrmann. *Angew. Chem., Int. Ed.* **38**, 2416 (1999); (c) N. Fröhlich, U. Pidun, M. Stahl, G. Frenking. *Organometallics* **16**, 442 (1997); (d) C. Boehme, G. Frenking. *Organometallics* **17**, 5801 (1998); (e) M.-T. Lee, C.-H. Hu. *Organometallics* **23**, 976 (2004).
26. (a) N. M. Scott, R. Dorta, E. D. Stevens, A. Correa, L. Cavallo, S. P. Nolan. *J. Am. Chem. Soc.* **127**, 3516 (2005); (b) H. Jacobsen. *J. Organomet. Chem.* **690**, 6068 (2005); (c) S. Diez-Gonzalez, S. P. Nolan. *Coord. Chem. Rev.* **251**, 874 (2007); (d) R. Tonner, G. Heydenrych, G. Frenking. *Chem. Asian J.* **2**, 1555 (2007); (e) U. Radius, F. M. Bickelhaupt. *Coord. Chem. Rev.* **253**, 678 (2009).
27. (a) F. Ramirez, N. B. Desai, B. Hansen, N. McKelvie. *J. Am. Chem. Soc.* **83**, 3539 (1961); (b) G. E. Hardy, J. I. Zink, W. C. Kaska, J. C. Baldwin. *J. Am. Chem. Soc.* **100**, 8002 (1978).
28. Recent reviews: (a) N. D. Jones, R. G. Cavell. *J. Organomet. Chem.* **690**, 5485 (2005); (b) O. I. Kolodiaznyi. *Phosphorous Ylides: Chemistry and Application in Organic Synthesis*, Wiley-VCH, Weinheim (1999); (c) O. I. Kolodiaznyi. *Tetrahedron* **52**, 1855 (1996); (d) A. W. Johnson (Ed.). *Ylides and Imines of Phosphorus*, John Wiley, New York (1993).
29. W. Petz, C. Kutschera, M. Heitbaum, G. Frenking, R. Tonner, B. Neumüller. *Inorg. Chem.* **44**, 1263 (2005).
30. J. Vicente, A. R. Singhal, P. G. Jones. *Organometallics* **21**, 5887 (2002).
31. W. Petz, F. Weller, J. Uddin, G. Frenking. *Organometallics* **18**, 619 (1999).
32. W. Petz, F. Öxler, B. Neumüller, G. Frenking, R. Tonner. Manuscript in preparation.
33. We calculated the second PE of **8** where one nitrogen atom is protonated instead of carbon. The calculated value is 11.6 kcal/mol smaller than the value for the carbon-diprotonated species.
34. (a) E. Oeser. *Chem. Ber.* **107**, 627 (1974); (b) M. J. Taylor, P. W. J. Surman, G. R. Clark. *J. Chem. Soc., Chem. Commun.* 2517 (1994).
35. N. Kuhn, G. Henkel, T. Kratz, J. Kreutzberg, R. Boese, A. H. Maulitz. *Chem. Ber.* **126**, 204 (1993).
36. N. Kuhn, T. Kratz, R. Boese, D. Bläser. *J. Organomet. Chem.* **470**, C8 (1994).
37. R. Dorta, E. D. Stevens, N. M. Scott, C. Costabile, L. Cavallo, C. D. Hoff, S. P. Nolan. *J. Am. Chem. Soc.* **127**, 2485 (2005).
38. K. E. Lewis, D. M. Golden, G. P. Smith. *J. Am. Chem. Soc.* **106**, 3905 (1984).
39. (a) S. Z. Goldberg, K. N. Raymond. *Inorg. Chem.* **12**, 2923 (1973); (b) W. Petz. Personal communication.
40. (a) T. Kappe, E. Ziegler. *Angew. Chem.* **86**, 529 (1974); (b) T. Kappe, E. Ziegler. *Angew. Chem., Int. Ed. Engl.* **13**, 491 (1974); (c) G. Paiaro, L. Pandolfo. *Comments Inorg. Chem.* **12**, 213 (1991).
41. J. J. Daly, P. Wheatley. *J. Chem. Soc.* 1703 (1966).
42. A. Ellern, T. Drews, K. Seppelt. *Z. Anorg. Allg. Chem.* **627**, 73 (2001).
43. M. Tanimoto, K. Kuchitsu, Y. Morino. *Bull. Chem. Soc. Jpn.* **43**, 2776 (1970).
44. N. Kuhn, M. Steimann, G. Weyers. *Z. Naturforsch., B* **54**, 427 (1999).
45. W. Petz, C. Kutschera, S. Tschan, F. Weller, B. Neumüller. *Z. Anorg. Allg. Chem.* **629**, 1235 (2003).
46. J. D. Walker, R. Poli. *Polyhedron* **8**, 1293 (1989).
47. N. Kuhn, H. Bohnen, T. Kratz, G. Henkel. *Liebigs Ann. Chem.* 1149 (1993).
48. H. C. Freeman, F. Huq, J. M. Rosalky, I. F. Taylor Jr. *Acta Crystallogr., Sect. B* **31**, 2833 (1975).