DOI: 10.1002/eiic.200801110

# Assessing the Potential of Zwitterionic NHC·CS<sub>2</sub> Adducts for Probing the **Stereoelectronic Parameters of N-Heterocyclic Carbenes**

Lionel Delaude,\*<sup>[a]</sup> Albert Demonceau,<sup>[a]</sup> and Johan Wouters<sup>[b]</sup>

Keywords: Betaines / Carbenes / Ligand effects / Nitrogen heterocycles / Zwitterions

Five imidazol(in)ium-2-dithiocarboxylates bearing cyclohexyl, mesityl, or 2,6-diisopropylphenyl substituents on their nitrogen atoms were prepared from the corresponding Nheterocyclic carbenes (NHCs) by reaction with carbon disulfide. They were characterized by IR, UV/Vis, and NMR spectroscopy, and by thermogravimetric analysis. Their molecular structures were determined by X-ray diffraction. For the sake of comparison, tricyclohexylphosphonium dithiocarboxylate was also examined. The data acquired were scrutinized to evaluate their usefulness for assessing the steric and electronic properties of NHC ligands. Because of their outstanding ability to crystallize, the five  $NHC \cdot CS_2$  betaines were found to be highly suitable for probing the steric influence of nitrogen atom substituents on imidazolylidene-based ligand precursors via XRD analysis, while the corresponding NHC·CO<sub>2</sub> adducts were deemed more appropriate for evaluating the  $\sigma$ -donating properties of carbene ligands.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2009)

### Introduction

Since they were first isolated and characterized by Arduengo and co-workers in 1991,<sup>[1]</sup> stable N-heterocyclic carbenes (NHCs) have been extensively studied.<sup>[2]</sup> Over the past 17 years, they have already afforded a whole new generation of nucleophilic reagents,<sup>[3]</sup> organocatalysts,<sup>[4]</sup> and organometallic catalysts,<sup>[5]</sup> including chiral ones,<sup>[6]</sup> which have revolutionized key areas of organic synthesis and polymer chemistry. Most NHCs investigated so far derive from 1H-imidazole. This electron-rich heterocycle provides a suitable framework that stabilizes the carbene center located between two nitrogen atoms.<sup>[7]</sup> Depending on the presence or the absence of a double bond between C4 and C5, imidazolin-2-ylidene and imidazolidin-2-ylidene species are obtained (Scheme 1).



Scheme 1. Stable NHCs derived from 1H-imidazole.

[b] Laboratoire de Chimie Biologique Structurale, Facultés Universitaires N.-D. de la Paix, 61 Rue de Bruxelles, 5000 Namur, Belgium



1882

Although most NHCs prepared so far (and/or immediate precursors or complexes derived thereof) were characterized by various analytical techniques,<sup>[8]</sup> general and efficient methods that would allow a detailed comparison of their steric and electronic properties are still missing.<sup>[9]</sup> This is in sharp contrast with the related class of phosphane ligands. Thanks to the pioneering work of Tolman,<sup>[10]</sup> cone angles  $(\theta)$  and carbonyl stretching vibration frequencies (v) are now routinely used to quantitatively assess the impact of substituents on phosphane ligands.<sup>[11]</sup> The usefulness of these parameters to predict structure-activity relationships is firmly established and has proven highly valuable in the rational design of new and improved phosphorus-based ligands for catalytic applications.[12]

In the case of NHC ligands, most efforts toward the definition of experimental parameters that would help compare different structures and permit a better assessment of the underlying steric and electronic factors originated from the group of Nolan. Initial work focused on calorimetric measurements during the reaction of [Cp\*RuCl]<sub>4</sub> with carbene ligands and X-ray diffraction studies of the resulting Cp\*Ru(NHC)Cl adducts. The two sets of data allowed, respectively, evaluation of the electron donor properties and the steric requirements of common imidazolin-2-ylidene ligands and their saturated analogues.<sup>[13]</sup> In 2005, Nolan et al. proposed another approach to obtain a more thorough understanding of the steric and electronic factors characterizing the NHC ligand class and to ease their comparison with the large array of data available for phosphanes. They investigated the reaction of Ni(CO)<sub>4</sub> with a range of  $\sigma$ -donor ligands. The IR v(CO) stretching vibration frequencies and the crystallographic structures of the  $Ni(CO)_{x}(NHC)$ 

<sup>[</sup>a] Center for Education and Research on Macromolecules (CERM), Institut de Chimie (B6a), Université de Liège, Sart-Tilman par, 4000 Liège, Belgium Fax: +32-4-3663497 E-mail: l.delaude@ulg.ac.be



adducts were determined. In combination with DFT calculations, they provided valuable information on the steric and electronic properties of NHCs.<sup>[14]</sup>

A closely related strategy was adopted by Herrmann and co-workers in 2006 to examine the ligand properties of prototypical carbenes based on various nitrogen ring systems. The Rh(COD)X(NHC) complexes (COD = 1,5-cyclooctadiene, X = Cl, I) were characterized by X-ray diffraction analysis, while the corresponding Rh(CO)<sub>2</sub>I(NHC) species served for IR measurements.<sup>[15]</sup> Other authors have relied on IR data of iron,<sup>[16]</sup> rhodium,<sup>[17]</sup> or iridium<sup>[18]</sup> carbonyl complexes to assess the overall donor strength of a carbene ligand. Pentacarbonyl complexes with the generic formula M(CO)<sub>5</sub>(NHC) based on group 6 transition metals (M = Cr, Mo, W) were also employed to determine the stretching frequency of the CO ligand trans to the NHC.<sup>[19]</sup> Unfortunately, changes in the metal nature and coordination sphere hinder comparison between the various data sets and no unified scale is presently available to evaluate the donor ability of NHCs.

Recent investigations from our laboratory<sup>[20]</sup> and from other groups<sup>[21,22]</sup> have shown that imidazol(in)ium-2carboxylates were labile zwitterionic adducts that could serve as carbene precursors for the preparation of late transition metal–NHC complexes, either preformed or generated in situ. In this contribution, we report on the synthesis and characterization of five imidazol(in)ium-2-dithiocarboxylates obtained by reacting free carbenes with CS<sub>2</sub> instead of CO<sub>2</sub>, a synthetic path first explored by Kuhn et al. in the late 1990s.<sup>[23,24]</sup> The influence of the nitrogen atom substituents and of the endocyclic C4–C5 double bond on their spectroscopic features was probed and we compare our findings with earlier results from the literature.

### **Results and Discussion**

#### Synthesis of Imidazol(in)ium-2-dithiocarboxylates

Currently, deprotonation of imidazol(in)ium chlorides or tetrafluoroborates with a strong base provides the most convenient and general access to NHCs, whether it is for preparative purposes<sup>[1,25]</sup> or for in situ catalytic applications.<sup>[18c,26]</sup> This is due, in part, to the availability of efficient and flexible synthetic procedures that allow the straightforward preparation of a wide range of imidazol-(in)ium salts from readily available acyclic precursors.<sup>[27]</sup> Thus, we chose this approach to release free carbenes in solution prior to their trapping with carbon disulfide. Alternative methods for generating NHC·CS<sub>2</sub> adducts include the cleavage of an enetetramine with carbon disulfide<sup>[28]</sup> or the displacement of chloroform by carbon disulfide upon thermolysis of a NHC·CHCl<sub>3</sub> adduct,<sup>[28c,29]</sup> but they both lack generality.

In practice, a set of five representative imidazol(in)ium chlorides was elected as starting materials (Scheme 2). These NHC precursors were suspended in dry THF and deprotonated with sodium hydride at room temperature. Other strong bases such as potassium hydride, potassium

*tert*-butoxide, or potassium bis(trimethylsilyl)amide were also tested and found equally suitable. The time needed to complete this step varied greatly from one experiment to another. In some cases, addition of a few drops of DMSO or tBuOH helped solubilize the reaction partners and hastened the release of free carbenes in solution. Recourse to imidazol(in)ium tetrafluoroborates instead of chlorides usually slowed down the reaction. The nature of the heterocycle (saturated imidazolinium salts are slightly less acidic than their unsaturated imidazolium counterparts).<sup>[19b,30]</sup> the steric bulk of the nitrogen substituents (2,6-diisopropylphenyl groups may restrain access of the base to the acidic C2-H center),<sup>[26d]</sup> and the influence of the inorganic counterion [imidazol(in)ium tetrafluoroborates often display a higher crystallinity and a lower solubility than analogous chlorides] must all intervene in a complex manner to explain the different rates of deprotonation observed.



Scheme 2. Synthesis of imidazol(in)ium-2-dithiocarboxylates used in this work.

Once the deprotonation step was completed, the suspensions were allowed to settle down and the inorganic byproduct (NaCl) was filtered off, along with any unreacted starting materials. A small excess of carbon disulfide was added at once to the free carbene solutions. It led to an instantaneous color change and to the rapid formation of zwitterionic adducts. 1,3-Dimesitylimidazolium-2-dithiocarboxylate (nicknamed IMes·CS<sub>2</sub>) and its saturated heterocycle analogue (nicknamed SIMes·CS<sub>2</sub>) precipitated from the reaction medium, whereas betaines bearing 2,6-diisopropylphenyl (IDip·CS<sub>2</sub> and SIDip·CS<sub>2</sub>) or cyclohexyl substituents (ICy·CS<sub>2</sub>) on their nitrogen atoms remained soluble in THF. The solvent was evaporated under reduced pressure

# FULL PAPER

to afford the zwitterionic products in solid form. Analytically pure samples suitable for X-ray diffraction analysis and characterization by various experimental techniques were further recrystallized from MeCN or EtOH (see Exp. Sect.).

Overall yields for the preparation of dithiocarboxylate adducts from imidazol(in)ium chlorides according to the in situ method described above were highly variable (Scheme 2). Nevertheless, the reaction between carbon disulfide and a free carbene always occurred rapidly and quantitatively at room temperature. Because of the remarkable tendency of the zwitterionic adducts to form crystalline materials, only minor losses were encountered during the final purification if recrystallization solvents are properly selected. The main cause for an unsatisfactory mass balance is a recalcitrant deprotonation step. This was evidenced by a control experiment in which the 1,3-dimesitylimidazolin-2-ylidene free carbene (IMes) was isolated and recrystallized prior to its reaction with carbon disulfide in THF. Under these conditions, the corresponding dithiocarboxylate was isolated in 91% yield, whereas the in situ deprotonation of IMes·HCl with NaH followed by filtration and direct addition of CS<sub>2</sub> afforded only a 55% isolated yield of IMes·CS<sub>2</sub>.

For the sake of comparison, the carbon disulfide adduct of tricylohexylphosphane was also prepared. It precipitated rapidly upon addition of CS<sub>2</sub> to an ethanolic solution of PCy<sub>3</sub> at room temperature and was isolated in high yield and purity by simple filtration and washing [Equation (1)]. This compound and other homologous trialkylphosphonium dithiocarboxylates such as Et<sub>3</sub>P·CS<sub>2</sub> or *n*Bu<sub>3</sub>P·CS<sub>2</sub> have been known in the literature for more than a hundred years.<sup>[31]</sup> Their zwitterionic nature is well established and they serve as versatile ligands in coordination chemistry.<sup>[32]</sup> It should be pointed out that less basic triarylphosphanes do not afford stable adducts with CS<sub>2</sub> alone, although incorporation of a Ph<sub>3</sub>P·CS<sub>2</sub> ligand coordinated as a  $\kappa^2$ -*S*,*S'* chelate was evidenced in cationic complexes of iridium<sup>[33]</sup> and iron.<sup>[34]</sup>

$$PCy_3 + CS_2 \xrightarrow{EtOH, r.t., 15 \text{ min}} Cy_3 \xrightarrow{P} \overset{S}{\swarrow} S$$

#### Characterization of Imidazol(in)ium-2-dithiocarboxylates

Various analytical techniques were employed to investigate the structural features of the five NHC·CS<sub>2</sub> and PCy<sub>3</sub>·CS<sub>2</sub> adducts under study. NMR spectroscopy unambiguously confirmed the identity of the hydrocarbon backbones but was of limited use to help rank the different carbene moieties in terms of stereoelectronic properties. This was due in part to the difficulty in finding a universal solvent that would dissolve all samples and allow a straightforward comparison of chemical shifts between compounds. CDCl<sub>3</sub> was a solvent of choice in many cases. However, IMes·CS<sub>2</sub> was only poorly soluble in this medium and required the use of more polar  $[D_6]DMSO$  instead.  $PCy_3 \cdot CS_2$ , on the other hand, was highly labile in solution and switching to less polar  $CD_2Cl_2$  containing a few drops of  $CS_2$  allowed one to prevent the release of free phosphane.

Monitoring the betaine formations by <sup>1</sup>H NMR spectroscopy revealed mainly the disappearance of the strongly deshielded (9-11 ppm) imidazol(in)ium H2 signals, while <sup>13</sup>C NMR spectra showed the emergence of new resonances at ca. 220–226 ppm for the dithiocarboxylate groups. The heterocyclic C2 carbon atom remained unaffected by changes in the substituents on the vicinal nitrogen atoms. Its signal was located at ca. 149 ppm in imidazolium-2-dithiocarboxylates and 165 ppm in their saturated imidazolinium counterparts (Table 1). Contrary to what was observed in imidazolium chlorides and free imidazolin-2-ylidenes, replacement of N-aryl substituents by better donor N-alkyl groups did not result in any significant upfield shift for C2 in imidazolium-2-dithiocarboxylates. This observation is not limited to cyclohexyl groups, since identical  $\delta_{C2}$  values of 149-150 ppm were reported by Kuhn et al. for 1,3-dimethyl, diethyl, diisopropyl, bis(2-methoxyethyl), and bis(3methoxypropyl)-4,5-dimethylimidazolium-2-dithiocarboxylates.<sup>[23]</sup> In <sup>31</sup>P NMR the signal for PCy<sub>3</sub>·CS<sub>2</sub> was found at  $\delta = 19$  ppm, intermediate between those recorded for the free phosphane ( $\delta = 11$  ppm) and its oxide ( $\delta = 51$  ppm), the two decomposition products that appeared when the NMR tube was exposed to air for a few hours.

Table 1. <sup>13</sup>C NMR chemical shifts of C2 in various imidazol(in)ium chlorides, NHCs, and imidazol(in)ium-2-dithiocarboxylates.

NHC·HCl	$\delta_{\mathrm{C2}}$ [ppm]	NHC	$\delta_{\mathrm{C2}}$ [ppm]	$\text{NHC}{\cdot}\text{CS}_2$	$\delta_{\mathrm{C2}}$ [ppm]
ICy•HCl	133.9 <sup>[a]</sup>	ICy	210.1 <sup>[b,e]</sup>	ICy•CS <sub>2</sub>	149.4 <sup>[d]</sup>
IMes•HCl	139.1 <sup>[a]</sup>	IMes	219.7 <sup>[b,f]</sup>	IMes·CS <sub>2</sub>	146.7 <sup>[a]</sup>
IDip•HCl	139.8 <sup>[a]</sup>	IDip	220.6 <sup>[c,g]</sup>	IDip•CS <sub>2</sub>	149.1 <sup>[d]</sup>
SIMes•HCl	160.2 <sup>[a]</sup>	SIMes	243.8 <sup>[c,g]</sup>	SIMes·CS <sub>2</sub>	165.0 <sup>[d]</sup>
SIDip•HCl	160.0 <sup>[a]</sup>	SIDip	244.0 <sup>[c,g]</sup>	SIDip•CS <sub>2</sub>	164.2 <sup>[d]</sup>

<sup>[</sup>a] Solvent:  $[D_6]DMSO$ . [b] Solvent:  $[D_8]THF$ . [c] Solvent:  $C_6D_6$ . [d] Solvent: CDCl<sub>3</sub>. [e] Data from ref.<sup>[51]</sup>. [f] Data from ref.<sup>[1b]</sup>. [g] Data from ref.<sup>[52]</sup>.

The FT-IR spectra of the five NHC·CS<sub>2</sub> and PCy<sub>3</sub>·CS<sub>2</sub> adducts were recorded in KBr pellets. Apart from the various C-H stretching vibration bands located between 2840 and 3100 cm<sup>-1</sup>, the two most intense absorptions were caused by the asymmetric stretching vibrations of the N<sub>2</sub>C<sup>+</sup> and  $CS_2^-$  groups (Table 2). The former endocyclic unit gave rise to a strong band in the 1470-1530 cm<sup>-1</sup> region, in accordance with previous experimental observations<sup>[35]</sup> and theoretical calculations.<sup>[36]</sup> This position is indicative of a double bond character within the  $N_2C^+$  group that can be easily rationalized by contribution of the canonical forms <sup>+</sup>N=C-N and N-C=N<sup>+</sup>. A second intense absorption in the 1050–1080 cm<sup>-1</sup> region was assigned to the  $CS_2^-$  group. Indeed, ab initio calculations for 1,3-dimethylimidazolinium-2-dithiocarboxylate predicted a 1041 cm<sup>-1</sup> wavenumber for  $v_{asym}(CS_2^{-})$ , in good agreement with the 1047 cm<sup>-1</sup> experimental value recorded.<sup>[36]</sup> Computations also showed that the corresponding symmetric stretching vibration was very weak and located below 900 cm<sup>-1</sup>, thereby precluding



Table 2. IR stretching v	vibrations for various	imidazol(in)ium-2-c	arboxylates and	-dithiocarboxylates.
--------------------------	------------------------	---------------------	-----------------	----------------------

NHC·CS <sub>2</sub>	$v_{asym}(N_2C^+)$ [cm <sup>-1</sup> ]	$v_{asym}(CS_2^{-})$ [cm <sup>-1</sup> ]	NHC·CO <sub>2</sub>	$v_{asym}(CO_2^{-}) \ [cm^{-1}]^{[a]}$
ICy•CS <sub>2</sub>	1474	1058	ICy•CO <sub>2</sub>	1663
$IMes \cdot CS_2$	1488	1052	IMes•CO <sub>2</sub>	1675
$IDip \cdot CS_2$	1469	1058	IDip•CO <sub>2</sub>	1679
SIMes·CS <sub>2</sub>	1531	1064	SIMes•CO <sub>2</sub>	1683
SIDip•CS <sub>2</sub>	1524	1080	SIDip•CO <sub>2</sub>	1684

[a] Data from ref.<sup>[20a]</sup>.

its identification with certainty. For the SIDip·CS<sub>2</sub> adduct, three distinct lines were clearly visible at 1045, 1062, and 1080 cm<sup>-1</sup>. We tentatively assigned the CS<sub>2</sub><sup>-</sup> asymmetric stretching vibration to the most intense one at 1080 cm<sup>-1</sup>, although this attribution remains questionable. A similar fine structure was also observed for PCy<sub>3</sub>·CS<sub>2</sub> at 1032, 1044, and 1053 cm<sup>-1</sup>. In this case, however, the three bands displayed similar intensities. This pattern was already reported in the literature<sup>[37]</sup> and is not unprecedented for trialkylphosphane–carbon disulfide adducts.<sup>[38]</sup> Comparison with the IR spectrum of free PCy<sub>3</sub> that displayed weak absorptions at 1030 and 1044 cm<sup>-1</sup> with a shoulder at 1049 cm<sup>-1</sup> did not help us locate unambiguously the band responsible for the asymmetric stretching vibration of the dithiocarboxylate anion in this inner salt.

All in all, neither the  $v_{asym}(N_2C^+)$  nor the  $v_{asym}(CS_2^-)$  IR stretching vibrations are satisfactory probes to compare the  $\sigma$ -donor strengths of NHCs. A much more convenient and reliable indirect measurement of the electron-donating properties of imidazolylidene ligands was achieved by monitoring the v<sub>asym</sub>(CO<sub>2</sub><sup>-</sup>) stretching vibration bands in imidazol(in)ium-2-carboxylates.<sup>[20a]</sup> In this case, strong absorption bands located in the  $1660-1690 \text{ cm}^{-1}$  region could be unambiguously assigned to the carboxylate group. ICy expected to be the most basic ligand due to its alkyl-substituted nitrogen atoms led to the lowest stretching wavenumber among the five NHC·CO<sub>2</sub> adducts investigated (Table 2). Aryl-substituted imidazolin-2-ylidene species IMes and IDip came next, closely followed by their imidazolidin-2-ylidene analogues SIMes and SIDip. Previous experimental results obtained when comparing the v(CO)stretching wavenumbers in Ni(CO)<sub>3</sub>(NHC) complexes also suggested that saturated NHC ligands were slightly less electron-donating than their unsaturated counterparts,<sup>[14]</sup> although examination of Rh(CO)<sub>2</sub>I(NHC) complexes<sup>[15]</sup> and determination of the relative bond dissociation enthalpies (BDE) in Cp\*Ru(NHC)Cl adducts<sup>[13]</sup> led to the opposite conclusion. Further theoretical,<sup>[39]</sup> spectroscopic,<sup>[40]</sup> and electrochemical<sup>[16,18d]</sup> studies have stressed the intervention of  $\pi$ -type contributions in addition to  $\sigma$ -donation in the bonding of NHCs to transition metals. Thus, several types of stereoelectronic metal-ligand interactions must intervene in a complex manner to determine the relative ranking of saturated and unsaturated carbene ligands. Measuring the value of  $v_{asym}(CO_2^{-})$  in NHC·CO<sub>2</sub> betaines provides a new, efficient approach to evaluate selectively the  $\sigma$ -donating properties of carbene ligands, since it does not involve any atom with d orbitals. Moreover, the experimental procedure is very easy to implement and does not require the use of highly toxic reagents such as carbon monoxide or nickel tetracarbonyl.

The UV/Vis spectra of the five NHC·CS<sub>2</sub> adducts were recorded in acetonitrile. They displayed absorption maxima in the 210-270 nm region that most likely originated from  $\pi \rightarrow \pi^*$  transitions within the (hetero)aromatic rings. They also showed a medium absorption above 300 nm ascribable to a  $\pi \rightarrow \pi^*$  transition in the CS<sub>2</sub><sup>-</sup> group.<sup>[36]</sup> The maximum wavelength for this band was located at 356 nm for ICy·CS<sub>2</sub>, 362 nm for SIMes·CS<sub>2</sub> and SIDip·CS<sub>2</sub>, and 364 nm for IMes·CS<sub>2</sub> and IDip·CS<sub>2</sub>, down from 366 nm in  $PCy_3 \cdot CS_2$ . Hence, substitution of the phosphane by a NHC induced only a minor hypsochromic shift. Yet it had a beneficial influence on the betaine lifetime in solution. Indeed, the NHC·CS<sub>2</sub> adducts remained stable for at least a week in acetonitrile, whereas PCy3•CS2 fully decomposed within one hour. This result contrasts with previous spectrophotometric measurements on the PEt<sub>3</sub>/CS<sub>2</sub> system that showed a complete displacement of the equilibrium depicted in Equation (2) toward adduct formation in acetonitrile.<sup>[41]</sup>

To probe the thermal stability of the five NHC·CS<sub>2</sub> and PCy<sub>3</sub>·CS<sub>2</sub> adducts in the solid state, we carried out thermogravimetric analysis (TGA). The results are depicted in Figure 1. The phosphane betaine was the least stable of the series and started losing weight at 58 °C, whereas imid-



Figure 1. TGA curves of the five NHC·CS<sub>2</sub> and PCy<sub>3</sub>·CS<sub>2</sub> adducts used in this work.

# FULL PAPER

azol(in)ium-2-dithiocarboxylates resisted decomposition until temperatures high above 100 °C. Degradation began at 164 °C for IMes·CS<sub>2</sub>, 177 °C for SIDip·CS<sub>2</sub>, 202 °C for ICy·CS<sub>2</sub>, 211 °C for IDip·CS<sub>2</sub>, and 225 °C for SIMes·CS<sub>2</sub>. Evidence for a clean loss of carbon disulfide was detected only with PCy<sub>3</sub>·CS<sub>2</sub> (theoretical weight loss: 21.35%, found 21.33%). This behavior reflects both the lability of the Cy<sub>3</sub>P<sup>+</sup>–CS<sub>2</sub><sup>-</sup> bond and the relative stability of tricyclohexylphosphane. Nucleophilic carbenes, on the other hand, form much more stable zwitterionic adducts with CS<sub>2</sub>, but once released they undergo rapid thermolysis.

### X-ray Diffraction Studies

Whereas the recrystallization of NHC·CO<sub>2</sub> compounds is hampered by the labile and sometimes hygroscopic nature of these adducts,<sup>[21,24,42]</sup> crystals of the five NHC·CS<sub>2</sub> betaines under investigation were easily grown by dissolving crude samples into a hot polar solvent, such as ethanol or acetonitrile, followed by slow evaporation of the saturated solutions in an open vessel at room temperature. Beautiful ruby-like specimens with dimensions reaching a few millimeters were obtained in most cases (Figure 2). Their molecular structures were determined by X-ray diffraction analysis (Figure 3). The crystal structure of PCy<sub>3</sub>·CS<sub>2</sub> had already been solved by Vittal and Dean in 1997.<sup>[43]</sup> Both ICy·CS<sub>2</sub> and IMes·CS<sub>2</sub> crystallized with two molecules in the asymmetric unit. For the sake of clarity, only one of them is depicted in Figure 3 that also shows the common atom numbering system adopted to ease comparison between the various structures. Selected bond lengths and angles are listed in Table 3.

Within each molecule, the C–S distances were similar, indicating that the negative charge was equally spread over the two sulfur atoms. This equivalence is best illustrated by the C<sub>2</sub> symmetry observed for all compounds. In the case of IMes·CS<sub>2</sub> and SIMes·CS<sub>2</sub>, only half of the molecules formed the asymmetric unit, the other half being generated by twofold axis (non-)crystallographic symmetry. The car-



Figure 2. Crystals of the five NHC·CS<sub>2</sub> adducts used in this work. Clockwise from top left corner: ICy·CS<sub>2</sub>, IMes·CS<sub>2</sub>, IDip·CS<sub>2</sub>, SIMes·CS<sub>2</sub>, SIDip·CS<sub>2</sub>, euro coin (23.25 mm diameter).



Figure 3. (a) Atom numbering system and ORTEP drawings of (b)  $ICy \cdot CS_2$ , (c)  $IMes \cdot CS_2$ , (d)  $SIMes \cdot CS_2$ , (e)  $IDip \cdot CS_2$ , (f)  $SIDip \cdot CS_2$  in the crystal. Thermal ellipsoids were set at the 50% probability level.

bon atom of the dithiocarboxylate group lay on a special crystallographic position and the second sulfur atom was

Table 3. Selected bond lengths	(Å) and angles	(°) derived from c	ystal structures of the fi	we NHC·CS <sub>2</sub> adducts used in	this work. <sup>[a</sup>
--------------------------------	----------------	--------------------	----------------------------	--	--------------------------

NHC·CS <sub>2</sub>	C6–S1	C6–S2	N1-C2	N1-C5	C4–C5	N1–C1a
ICy•CS <sub>2</sub>	1.656(3)	1.641(2)	1.335(3)	1.379(3)	1.329(4)	1.479(3)
• -	1.652(3)	1.657(3)	1.335(3)	1.377(3)	1.333(3)	1.478(3)
IMes·CS <sub>2</sub>	1.667(3)	1.667(3)	1.374(6)	1.374(6)	1.341(10)	1.456(6)
	1.669(3)	1.669(3)	1.387(6)	1.387(6)	1.318(11)	1.461(6)
IDip·CS <sub>2</sub>	1.676(3)	1.659(5)	1.341(2)	1.387(1)	1.333(2)	1.452(2)
SIMes·CS <sub>2</sub>	1.662(2)	1.662(2)	1.315(4)	1.480(5)	1.521(8)	1.446(4)
SIDip·CS <sub>2</sub>	1.665(2)	1.651(2)	1.326(2)	1.471(1)	1.510(2)	1.447(2)
NHC·CS <sub>2</sub>	C2–C6	N1-C2-N3	S1-C6-S2	N1-C2-C6-S1	N1-C2-C6-S2	C1b-C1a-N1-C2
ICy·CS <sub>2</sub>	1.489(3)	108.1(2)	130.3(1)	-95.2(3)	84.2(3)	-144.4(3)
-	1.483(3)	107.9(2)	130.2(1)	-91.6(3)	87.0(3)	-110.6(3)
IMes·CS <sub>2</sub>	1.489(7)	122.2(4)	129.1(4)	-65.3(2)	118.0(5)	104.9(6)
	1.483(8)	106.4(5)	129.1(4)	-62.1(2)	114.7(5)	106.6(6)
IDip·CS <sub>2</sub>	1.487(2)	107.5(1)	128.5(2)	85.9(2)	93.2(2)	95.9(2)
SIMes·CS <sub>2</sub>	1.502(6)	112.0(4)	130.3(3)	92.4(2)	92.8(5)	94.4(5)
SIDip·CS <sub>2</sub>	1.495(2)	111.6(1)	131.5(2)	92.0(2)	-88.0(2)	84.6(2)

[a] See Figure 3 (a) for atom numbering.

generated by symmetry from the coordinates of the first one, leading to identical C–S bonds. Furthermore, the lengths of the two C–S bonds were much closer to the distances observed for common C=S double bonds (1.67 Å) than for single C–S bonds (1.75 Å).<sup>[44]</sup> For all five crystal structures, the N1–C2 and N3–C2 bond lengths were also (nearly) equal and in the range 1.32–1.49 Å (Table 3). This indicates a significant C=N double-bond character, consistent with electronic conjugation within the N<sub>2</sub>C<sup>+</sup> motif. Such a delocalization is in agreement with previous studies on related crystal structures<sup>[36]</sup> and correlates well with the strong absorption band observed in the 1470–1530 cm<sup>-1</sup> region of the FT-IR spectra (vide supra).

Within the heterocyclic rings, the C4-C5 distance corresponded to a single C-C bond in the imidazolinium rings [SIMes·CS<sub>2</sub>: 1.521(8) Å, SIDip·CS<sub>2</sub>: 1.510(2) Å], whereas it was significantly shorter in the imidazolium rings [ICy•CS<sub>2</sub>: 1.329(4) and 1.333(3) Å, IMes·CS<sub>2</sub>: 1.341(10) and 1.318(11) Å, IDip•CS<sub>2</sub>: 1.333(2) Å]. For these aromatic compounds, delocalization in the whole five-membered ring was also underlined by shorter N1-C5 and N3-C4 bonds (Table 3). Influence of the various nitrogen substituents on the electronic delocalization of the imidazol(in)ium heterocycles was limited. Indeed, similar geometries were observed for ICy·CS<sub>2</sub>, IMes·CS<sub>2</sub>, and IDip·CS<sub>2</sub>. Thus, electronic effects of the substituted phenyl rings are not transferred to the central imidazole moiety. This was underlined by the rather long N-C inter-ring distances N1-C1a and N3–C3a (see Table 3), closer to a single N–C bond (1.47 Å) than to a N=C double bond (1.34 Å).[44] Lack of delocalization is a consequence of the perpendicularity between the N-substituting groups and the imidazol(in)ium rings (see torsion angle C1b-C1a-N1-C2 in Table 3).

In all five crystal structures, the imidazol(in)ium rings and the dithiocarboxylate unit were nearly orthogonal with torsion angles N1–C2–C6–S1 close to 90° (Table 3). Similar conformations were also observed in acyclic carbeniun dithiocarboxylates<sup>[45]</sup> and in all but one of the other imidazol(in)ium-2-carboxylates<sup>[21,24]</sup> and their dithio<sup>[23,28,36,46]</sup> or diseleno<sup>[36]</sup> analogues investigated so far by XRD analysis (Scheme 3). Only in 1,3-dimethylimidazolium-2-carboxylate were the imidazolium and the carboxylate groups almost coplanar, with a twist angle of 29°. In this case, steric requirements from both the nitrogen substituents and the CX<sub>2</sub> moiety were minimized, allowing the formation of hydrogen-bonded sheets with a dense columnar  $\pi$ - $\pi$  stacking in the crystal structure.<sup>[42]</sup>



Scheme 3. Orthogonal disposition of the  $N_2C^+$  and  $CX_2^-$  units in various zwitterionic compounds.



The rather long C2–C6 distances [between 1.483(3) and 1.502(6) Å] confirmed the poor electronic communication between the delocalized CS<sub>2</sub> moiety and the imidazol(in)ium ring. The perpendicular arrangement between the  $CS_2^{-1}$ and  $N_2C^+$  parts is probably retained in solution, as proposed by Nakayma et al. for 1,3-dimethylimidazolinium dithio-, diseleno-, and thioselenocarboxylates on the grounds of <sup>1</sup>H NMR spectroscopic data and ab initio calculations.<sup>[36]</sup> Through-space attractive Coulombic interactions between the carbenium ion carbon and the lone pair of electrons on the sulfur atoms were held responsible for this situation. In addition, incorporation of bulky aryl substituents, such as 1,3-bis(2,4,6-trimethylphenyl) or 1,3-bis(2,6-diisopropylphenyl) groups on the nitrogen atoms should further stabilize a perpendicular disposition of the carbenium or imidazol(in)ium and dithiocarboxylate ions by steric effects.

#### **Computational Analysis**

In order to quantify the steric demand of NHC ligands, Cavallo and Nolan have defined a  $V_{Bur}$  parameter that corresponds to the portion of a 3-Å radius coordination sphere centered on a metal atom, buried by overlap with atoms of the ligand (Figure 4).<sup>[14,47]</sup> Because of the highly asymmetric geometry of imidazole-based carbenes that usually display a much larger wingspan along the axis defined by the two nitrogen exocyclic substituents than in the direction perpendicular to the central heterocyclic ring, this model allows for a more realistic comparison with other ligands, particularly tertiary phosphanes, than the Tolman cone angle ( $\theta$ ).<sup>[10]</sup> The bulkier a specific ligand is, the greater its  $V_{Bur}$ .



Figure 4. Schematic representation of the sphere dimensions used for the determination of the  $\% V_{\rm Bur}$  steric parameter.

The values of  $V_{Bur}$  extracted from the X-ray crystal structures of the five NHC·CS<sub>2</sub> adducts used in this work are listed in Table 4 along with the data obtained from the molecular structure of PCy<sub>3</sub>·CS<sub>2</sub>. The dummy metal center defining the origin of the sphere was placed at 2.0 Å from the coordinating C or P atom. This arbitrary distance is typical for a metal–NHC bond, such as those recorded previously in Cp\*Ru(NHC)Cl,<sup>[5b]</sup> Rh(COD)X(NHC) (X = Cl, I),<sup>[15]</sup> or Ni(CO)<sub>x</sub>(NHC) complexes.<sup>[14]</sup> Putting the reference atom at 1.5 Å from the ligand, which is the average C2–C6 bond length observed between the imidazol(in)ium and dithiocarboxylate units of NHC·CS<sub>2</sub> betaines (cf. Table 3) afforded higher values of  $V_{Burb}$  but the evolution within the series was not drastically altered.

Table 4. Steric parameter	$\% V_{\rm Bur}$	for the	five	NHC	ligands	and	PCy <sub>3</sub>
used in this work.							

Ligand (L)	$%V_{\text{Bur}}$ computed from $L \cdot CS_2$	$%V_{Bur}$ computed from Ni(CO) <sub>3</sub> (L) <sup>[a]</sup>
ICy	24	23
IMes	27	26
SIMes	26	27
IDip	26	29
SIDip	27	30
PCy <sub>3</sub>	34	32

[a] Data from ref.<sup>[47]</sup>

Because the different figures gathered in Table 4 are close to each other, great care should be taken in their interpretation. Yet, recent investigations by Cavallo and co-workers showed that  $\% V_{\rm Bur}$  values could be reasonably trusted to rationalize NHC dimerization energies<sup>[48]</sup> or binding energies of NHC ligands in Cp\*Ru(NHC)Cl complexes.<sup>[49]</sup> The data obtained in the present study are in rather good agreement with those previously computed from  $Ni(CO)_x(NHC)$ complexes (Table 4).<sup>[47]</sup> However, the  $%V_{Bur}$  values derived from NHC·CS<sub>2</sub> adducts suggest that saturated or unsaturated carbenes bearing mesityl or 2,6-diisopropylphenyl substituents possess rather similar footprints, whereas the IDip and SIDip ligands were always found to be slightly more sterically demanding than IMes and SIMes when metal-NHC complexes served as templates. This small discrepancy is due to minor changes in the orientation of the aryl substituents relative to the central imidazole ring in order to accommodate the steric pressure exerted by the CS<sub>2</sub> unit on the NHC moiety. Variations of packing forces in the different types of crystals should also be taken into consideration. As a matter of fact, several structural investigations have evidenced the high flexibility of the nitrogen exocyclic substituents within NHC ligands in response to subtle changes of environment.<sup>[18d,50]</sup>

### **Conclusion and Perspectives**

A range of imidazol(in)ium chlorides were converted into the corresponding 2-dithiocarboxylates by a two-step procedure involving in situ generation of free carbenes with a strong base followed by trapping with carbon disulfide. The resulting zwitterionic products were stable, crystalline solids. They were characterized by various analytical techniques, including IR, UV/Vis, and NMR spectroscopy, and their molecular structures were determined by X-ray diffraction analysis. The data acquired were scrutinized to evaluate their usefulness for assessing the steric and electronic properties of NHC ligands. Because of their outstanding ability to crystallize, NHC·CS<sub>2</sub> betaines are promising candidates to probe the steric influence of nitrogen substituents on imidazolylidene-based ligand atom precursors via XRD analysis. Difficulties in locating the  $v_{asym}(CS_2^{-})$  stretching vibration band in IR spectroscopy complicates, however, their use to quantify the electron-donating properties of N-heterocyclic carbenes. For this purpose, measuring the analogous  $v_{asym}(CO_2^{-})$  band in the IR

spectra of  $NHC \cdot CO_2$  adducts provides a more convenient and reliable approach.

As a follow-up to this study, we are currently synthesizing other NHC·CS<sub>2</sub> adducts from known or new imidazol(in)ium salts in order to determine their structure by X-ray crystallography. This would enlarge the set of data available for comparison and ranking of NHC precursors in terms of steric requirements. Additionally, we envision to take advantage of the fast and irreversible trapping of free carbenes by carbon disulfide to form stable, colored, welldefined adducts for analytical or preparative purposes. Thus, we believe that CS<sub>2</sub> could serve as a nonprotic quenching agent for catalytic systems involving free carbenes or that it could help bring to light the involvement of such highly active species during mechanistic investigations.

## **Experimental Section**

General: All syntheses were carried out under a dry argon atmosphere using standard Schlenk techniques. Solvents were distilled from appropriate drying agents and deoxygenated prior to use. Imidazol(in)ium salts ICy·HCl,<sup>[51]</sup> IMes·HCl,<sup>[52]</sup> IDip·HCl,<sup>[52]</sup> SIMes·HCl,<sup>[52]</sup> and SIDip·HCl<sup>[52]</sup> were synthesized according to published procedures. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at 298 K with a Bruker DRX 400 spectrometer operating at 400.13 and 100.62 MHz, respectively. Chemical shifts are listed in parts per million downfield from TMS and are referenced from the solvent peaks or TMS. <sup>31</sup>P NMR spectra were recorded at 298 K with a Bruker Avance 250 spectrometer operating at 101.25 MHz with H<sub>3</sub>PO<sub>4</sub> as the external reference. Infrared spectra were recorded with a Perkin-Elmer Spectrum One FT-IR spectrometer. UV/Vis spectra were recorded with a Hewlett-Packard HP 8453 spectrophotometer. Thermogravimetric analyses were performed with a TA Q500 instrument using a 5 °C/min ramp. Melting points were recorded with an Electrothermal 9100 apparatus and are not corrected. Elemental analyses were carried out in the Laboratory of Pharmaceutical Chemistry at the University of Liège.

Preparation of Imidazol(in)ium-2-dithiocarboxylates: An oven-dried 100-mL round-bottomed flask equipped with a magnetic stirring bar and capped with a three-way stopcock was charged with imidazol(in)ium chloride (5 mmol) and 95% sodium hydride (0.1516 g, 6 mmol). The reactor was purged of air by applying three vacuum/ argon cycles before dry THF (50 mL) was added. The mixture was stirred at room temperature until the deprotonation step seemed to be complete (20 min to overnight). In some cases, a few drops of tBuOH or DMSO were added to induce the process. After the solid had settled down, the supernatant solution was filtered trough Celite and transferred with a cannula under an inert atmosphere into a two-neck 100-mL round-bottomed flask equipped with a magnetic stirring bar and capped with a three-way stopcock. Carbon disulfide (0.4 mL, 6.7 mmol) was added with a syringe. The color of the solution changed instantaneously. After 30 min of stirring at room temperature, the solvent was evaporated under vacuum. The residue was brought back to air and washed with n-pentane (10 mL). It was dried under high vacuum and recrystallized.

**1,3-Dicyclohexylimidazolium-2-dithiocarboxylate** (ICy·CS<sub>2</sub>): Dark red crystals (from EtOH). Yield 61% (0.65 g); m.p. 230–232 °C (dec.). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.14–1.26 (m, 2 H, Cy), 1.34–1.41 (m, 4 H, Cy), 1.47–1.57 (m, 4 H, Cy), 1.71–1.75 (br. d, 2 H, Cy), 1.85–1.88 (br. d, 4 H, Cy), 2.24–2.27 (br. d, 4 H, Cy),



4.51 (m, 2 H, CHN), 6.99 (s, 2 H, =CHN) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 25.0 (CH<sub>2</sub>), 25.2 (CH<sub>2</sub>), 32.3 (CH<sub>2</sub>), 57.5 (CHN), 115.1 (Im-C4,5), 149.4 (Im-C2), 226.0 (CS<sub>2</sub>) ppm. IR (KBr):  $\tilde{v}$  = 3090 (m), 2934 (s), 2855 (s), 1570 (m), 1474 (m), 1447 (m), 1249 (m), 1200 (m), 1058 (s), 901 (m) cm<sup>-1</sup>. UV/Vis (CH<sub>3</sub>CN):  $\lambda_{max}$  ( $\varepsilon$ ) = 217 (12500), 264 (6200), 356 nm (12800 m<sup>-1</sup> cm<sup>-1</sup>). C<sub>16</sub>H<sub>24</sub>N<sub>2</sub>S<sub>2</sub> (308.51): calcd. C 62.29, H 7.84, N 9.08, S 20.79; found C 62.38, H 8.07, N 9.22, S 20.86.

**1,3-Bis(2,4,6-trimethylphenyl)imidazolium-2-dithiocarboxylate** (**IMes·CS**<sub>2</sub>): Dark purple crystals (from MeCN). Yield 55% (1.06 g); m.p. 318 °C (dec.). <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>]DMSO):  $\delta$  = 2.23 (s, 12 H, *ortho*-CH<sub>3</sub>), 2.28 (s, 6 H, *para*-CH<sub>3</sub>), 7.03 (s, 4 H, *meta*-CH), 7.84 (s, 2 H, =CHN) ppm. <sup>13</sup>C NMR (100 MHz, [D<sub>6</sub>]-DMSO):  $\delta$  = 18.1 (*ortho*-CH<sub>3</sub>), 20.5 (*para*-CH<sub>3</sub>), 121.2 (Im-C4,5), 129.0 (*meta*-CH), 131.1 (C<sub>ar</sub>), 135.3 (C<sub>ar</sub>), 139.8 (C<sub>ar</sub>), 146.7 (Im-C2), 221.6 (CS<sub>2</sub>) ppm. IR (KBr):  $\tilde{v}$  = 3178 (m), 3154 (m), 2947 (w), 2918 (m), 1637 (w), 1615 (m), 1563 (m), 1488 (s), 1460 (s), 1379 (m), 1223 (s), 1166 (m), 1105 (m), 1073 (m), 1052 (s), 931 (m) cm<sup>-1</sup>. UV/Vis (CH<sub>3</sub>CN):  $\lambda_{max}$  ( $\varepsilon$ ) = 213 (31500), 255 (8000), 364 nm (8300 m<sup>-1</sup> cm<sup>-1</sup>). C<sub>22</sub>H<sub>24</sub>N<sub>2</sub>S<sub>2</sub> (380.58): calcd. C 69.43, H 6.36, N 7.36, S 16.85; found C 69.21, H 6.41, N 7.50, S 16.79.

**1,3-Bis(2,6-diisopropylphenyl)imidazolium-2-dithiocarboxylate** (**IDip·CS**<sub>2</sub>): Orange red crystals (from MeCN). Yield 89% (2.02 g); m.p. 294 °C (dec.). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.15 [d, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz, 12 H, CH(CH<sub>3</sub>)<sub>2</sub>], 1.33 [d, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz, 12 H, CH(CH<sub>3</sub>)<sub>2</sub>], 3.00 [sept, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz, 4 H, CH(CH<sub>3</sub>)<sub>2</sub>], 7.01 (s, 2 H, =CHN), 7.23 (d, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz, 4 H, *meta*-CH), 7.43 (t, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz, 2 H, *para*-CH) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 22.8 (CH<sub>3</sub>), 26.0 (CH<sub>3</sub>), 29.5 [(CH<sub>3</sub>)<sub>2</sub>CH], 120.6 (Im-C4,5), 124.6 (*meta*-CH), 130.8 (*ipso*-C), 131.4 (*para*-CH), 146.5 (*ortho*-C), 149.1 (Im-C2), 219.7 ppm. (CS<sub>2</sub>). IR (KBr):  $\tilde{v}$  = 3163 (w), 3059 (m), 2965 (s), 2928 (m), 2866 (m), 1557 (m), 1469 (s), 1383 (m), 1363 (m), 1331 (m), 1210 (m), 1180 (m), 1058 (s), 947 (m) cm<sup>-1</sup>. UV/Vis (CH<sub>3</sub>CN):  $\lambda_{max}$  ( $\varepsilon$ ) = 213 (25200), 261 (7900), 364 nm (8400 m<sup>-1</sup>cm<sup>-1</sup>). C<sub>28</sub>H<sub>36</sub>N<sub>2</sub>S<sub>2</sub> (464.74): calcd. C 72.36, H 7.81, N 6.03, S 13.80; found C 72.13, H 8.18, N 6.30, S 14.18.

**1,3-Bis(2,4,6-trimethylphenyl)imidazolinium-2-dithiocarboxylate** (SIMes-CS<sub>2</sub>): Orange crystals (from MeCN). Yield 77% (1.47 g); m.p. 296 °C (dec.). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.19 (s, 6 H, *para*-CH<sub>3</sub>), 2.54 (s, 12 H, *ortho*-CH<sub>3</sub>), 4.20 (s, 4 H, CH<sub>2</sub>), 6.87 (s, 4 H, *meta*-CH) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 19.7 (*ortho*-CH<sub>3</sub>), 21.9 (*para*-CH<sub>3</sub>), 49.9 (CH<sub>2</sub>N), 130.7 (*meta*-CH), 131.6 (*ipso*-C), 137.4 (*ortho*-C), 140.8 (*para*-C), 165.0 (Im-C2), 222.7 (CS<sub>2</sub>) ppm. IR (KBr):  $\tilde{v}$  = 2947 (w), 2915 (m), 2855 (w), 1609 (m), 1531 (s), 1465 (m), 1377 (m), 1351 (w), 1267 (s), 1211 (w), 1173 (w), 1064 (s), 856 (m) cm<sup>-1</sup>. UV/Vis (CH<sub>3</sub>CN):  $\lambda_{max}$  ( $\varepsilon$ ) = 216 (32000), 262 (8400), 362 nm (8200 m<sup>-1</sup>cm<sup>-1</sup>). C<sub>22</sub>H<sub>26</sub>N<sub>2</sub>S<sub>2</sub> (382.59): calcd. C 69.07, H 6.85, N 7.32, S 16.76; found C 69.53, H 7.07, N 7.58, S 16.98.

**1,3-Bis(2,6-diisopropylphenyl)imidazolinium-2-dithiocarboxylate** (**SIDip·CS**<sub>2</sub>): Orange red crystals (from MeCN). Yield 0.79 g (34%); m.p. 268–269 °C (dec.). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.28 [d, <sup>3</sup>J<sub>HH</sub> = 6.4 Hz, 12 H, CH(CH<sub>3</sub>)<sub>2</sub>], 1.38 [d, <sup>3</sup>J<sub>HH</sub> = 6.4 Hz, 12 H, CH(CH<sub>3</sub>)<sub>2</sub>], 3.47 [sept, <sup>3</sup>J<sub>HH</sub> = 6.4 Hz, 4 H, CH(CH<sub>3</sub>)<sub>2</sub>], 4.41 (s, 4 H, CH<sub>2</sub>), 7.16 (d, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz, 4 H, *meta*-CH), 7.31 (t, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, 2 H, *para*-CH) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 23.8 (CH<sub>3</sub>), 26.6 (CH<sub>3</sub>), 29.4 [(CH<sub>3</sub>)<sub>2</sub>CH], 51.4 (CH<sub>2</sub>N), 125.0 (*meta*-CH), 130.6 (*para*-CH), 130.7 (*ipso*-C), 147.5 (*ortho*-C), 164.2 (Im-C2), 219.8 (CS<sub>2</sub>) ppm. IR (KBr):  $\tilde{v}$  = 2965 (s), 2923 (m), 2865 (m), 1590 (w), 1524 (s), 1502 (sh), 1461 (m), 1441 (m), 1381 (m), 1356 (m), 1328 (m), 1281 (m), 1191 (m), 1080 (s), 1062 (m), 1045 (m), 937 (w) cm<sup>-1</sup>. UV/Vis (CH<sub>3</sub>CN):  $\lambda_{max}$  ( $\varepsilon$ ) = 216 (31300), 266

(11200), 362 nm (9000  $M^{-1}$  cm<sup>-1</sup>). C<sub>28</sub>H<sub>38</sub>N<sub>2</sub>S<sub>2</sub> (466.74): calcd. C 72.05, H 8.21, N 6.00, S 13.74; found C 72.05, H 8.08, N 6.79, S 14.29.

Preparation of Tricyclohexylphosphonium Dithiocarboxylate (PCy<sub>3</sub>·CS<sub>2</sub>): An oven-dried 100-mL round-bottomed flask equipped with a magnetic stirring bar and capped with a three-way stopcock was charged with tricyclohexylphosphane (1.40 g, 5 mmol). The reactor was purged of air by applying three vacuum/ argon cycles before degassed EtOH (25 mL) was added. Carbon disulfide (0.4 mL, 6.7 mmol) was syringed into the clear solution and it was stirred at room temperature. A precipitate appeared within a few seconds. After 15 min, the resulting suspension was brought back to air and filtered with suction. The precipitate was washed with EtOH (5 mL) and dried under high vacuum to afford the title compound as a brick powder (1.43 g, 83%); m.p. 119 °C (dec.), ref.<sup>[53]</sup> 118 °C. <sup>1</sup>H NMR (400 MHz,  $CD_2Cl_2 + CS_2$ ):  $\delta =$ 1.12-1.33 (m, 9 H, Cy), 1.54-1.64 (m, 6 H, Cy), 1.68-1.76 (m, 3 H, Cy), 1.78–1.86 (m, 6 H, Cy), 1.88–1.97 (m, 6 H, Cy), 2.84–2.94 (q, 3 H, CHP) ppm. <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub> + CS<sub>2</sub>):  $\delta$  = 26.1 (Cy-C4), 26.9 (Cy-C3), 27.4 (d,  $J_{CP}$  = 11.10 Hz, Cy-C2), 32.6 (d,  $J_{\rm CP} = 38.7$  Hz, Cy-C1), 225.9 (d,  $J_{\rm CP} = 31.10$  Hz, CS<sub>2</sub>) ppm. <sup>31</sup>P NMR (101 MHz,  $CD_2Cl_2 + CS_2$ ):  $\delta = 19$  ppm. IR (KBr):  $\tilde{v} = 2934$ (s), 2850 (s), 1637 (m), 1446 (m), 1297 (m), 1178 (m), 1053 (s), 1044 (m), 1031 (s), 1002 (m), 918 (w) cm<sup>-1</sup>. UV/Vis (CH<sub>3</sub>CN):  $\lambda_{max}$  ( $\varepsilon$ )  $= 221 (6400), 366 \text{ nm} (2000 \text{ M}^{-1} \text{ cm}^{-1}).$ 

X-ray Crystal Structure Determinations: Data were collected with an Enraf–Nonius CAD-4 diffractometer at room temperature. Cell parameters were determined from 25 well-centered reflections. Data collection program: CAD4-Mach3, data reduction: Helena, structure solution: SHELXS, structure refinement: SHELXL-97 (on  $F^2$ ),<sup>[54]</sup> data analysis: PLATON.<sup>[55]</sup> Reflections were corrected for Lorentz and polarization effects. Analytical correction was applied to correct for absorption effects. The quality of structure for IMes•CS<sub>2</sub> was poor despite efforts to improve its quality. It was, however, included for comparison.

CCDC-645144 (for  $ICy \cdot CS_2$ ), -645145 (for  $IMes \cdot CS_2$ ), -645146 (for  $SIMes \cdot CS_2$ ), -645147 (for  $IDip \cdot CS_2$ ), -645148 (for  $SIDip \cdot CS_2$ ), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

**ICy·CS<sub>2</sub>:** Dark red crystals (from EtOH) with dimensions  $0.22 \times 0.12 \times 0.05$  mm, triclinic,  $P\bar{1}$ , a = 9.699(2), b = 13.440(2), c = 14.367(4) Å, a = 109.87(2),  $\beta = 94.23(1)$ ,  $\gamma = 100.31(3)^{\circ}$ , V = 1714.4(7) Å<sup>3</sup>, Z = 4,  $\rho_{calcd} = 1.195$  gcm<sup>-3</sup>,  $F_{000} = 664$ ,  $\lambda$  Cu- $K_a = 1.54179$  Å,  $\theta_{max} = 75.01^{\circ}$ ,  $\omega/2\theta$  scan mode, 7043 independent reflections ( $R_{int} = 0.0153$ ), 4263 observed reflections [ $I > 2\sigma(I)$ ],  $\mu = 2.739$  mm<sup>-1</sup>,  $T_{min} = 0.5840$ ,  $T_{max} = 0.8752$ , 361 parameters,  $R_1$  (all data) = 0.1076,  $R_1$  (observed data) = 0.0491, S = GooF = 1.025,  $\Delta/s.u. = 0.000$ , residual  $\rho_{max} = 0.302$  eÅ<sup>-3</sup>.

**IMes·CS<sub>2</sub>:** Dark purple crystals (from MeCN) with dimensions  $0.22 \times 0.40 \times 0.42$  mm, monoclinic, P2/c, a = 14.854(10), b = 7.810(10), c = 17.565(10) Å,  $\beta = 92.3(4)^\circ$ , V = 2036(3) Å<sup>3</sup>, Z = 4,  $\rho_{calcd} = 1.241$  g cm<sup>-3</sup>,  $F_{000} = 808$ ,  $\lambda$  Cu- $K_a = 1.54179$  Å,  $\theta_{max} = 75.10^\circ$ ,  $\omega/2\theta$  scan mode, 4183 independent reflections ( $R_{int} = 0.0405$ ), 3672 observed reflections [ $I > 2\sigma(I)$ ],  $\mu = 2.412$  mm<sup>-1</sup>,  $T_{min} = 0.4306$ ,  $T_{max} = 0.6189$ , 243 parameters,  $R_1$  (all data) = 0.1197,  $R_1$  (observed data) = 0.1103, S = GooF = 2.410,  $\Delta/s.u. = 0.00$ , residual  $\rho_{max} = 1.076$  e Å<sup>-3</sup>.

**IDip·CS<sub>2</sub>:** Orange-red crystals (from MeCN) with dimensions  $0.20 \times 0.26 \times 0.26$  mm, monoclinic,  $P2_1/c$ , a = 13.222(2), b = 14.944(2), c = 15.124(3) Å,  $\beta = 110.8(1)^\circ$ , V = 2793.6(9) Å<sup>3</sup>, Z = 4,

 $\rho_{\text{calcd}} = 1.105 \text{ g cm}^{-3}, F_{000} = 1000, \lambda \text{ Cu-}K_a = 1.54179 \text{ Å}, \theta_{max} = 75.04^{\circ}, \omega/2\theta$  scan mode, 5756 independent reflections ( $R_{\text{int}} = 0.0232$ ), 5197 observed reflections [ $I > 2\sigma(I)$ ],  $\mu = 1.837 \text{ mm}^{-1}$ ,  $T_{\text{min}} = 0.6467, T_{\text{max}} = 0.7102, 315$  parameters,  $R_1$  (all data) = 0.0441,  $R_1$  (observed data) = 0.0396,  $S = GooF = 1.035, \Delta/\text{s.u.} = 0.002$ , residual  $\rho_{\text{max}} = 0.187 \text{ eÅ}^{-3}$ .

**SIMes·CS<sub>2</sub>:** Orange crystals (from MeCN) with dimensions 0.17 × 0.20 × 0.30 mm, orthorhombic, C222<sub>1</sub>, *a* = 7.626(1), *b* = 16.761(2), *c* = 16.312(2) Å, *V* = 2085.0(4) Å<sup>3</sup>, *Z* = 4,  $\rho_{calcd}$  = 1.219 gcm<sup>-3</sup>, *F*<sub>000</sub> = 816,  $\lambda$  Cu-*K<sub>a</sub>* = 1.54179 Å,  $\theta_{max}$  = 74.92°,  $\omega/2\theta$  scan mode, 1236 independent reflections (*R*<sub>int</sub> = 0.0155), 1106 observed reflections [*I* > 2 σ(*I*)],  $\mu$  = 1.837 mm<sup>-1</sup>, *T*<sub>min</sub> = 0.600, *T*<sub>max</sub> = 0.743, 122 parameters, *R*<sub>1</sub> (all data) = 0.0586, *R*<sub>1</sub> (observed data) = 0.0509, *S* = *GooF* = 1.102,  $\Delta$ /s.u. = 0.006, residual  $\rho_{max}$  = 0.348 eÅ<sup>-3</sup>.

**SIDip**-CS<sub>2</sub>: Orange-red crystals (from MeCN) with dimensions  $0.45 \times 0.35 \times 0.30$  mm, orthorhombic, *Pnma*, a = 12.510(6), b = 20.498(8), c = 10.544(3) Å, V = 2703.8(18) Å<sup>3</sup>, Z = 4,  $\rho_{calcd} = 1.147$  g cm<sup>-3</sup>,  $F_{000} = 1008$ ,  $\lambda$  Cu- $K_a = 1.54179$  Å,  $\theta_{max} = 74.89^{\circ}$ ,  $\omega/2\theta$  scan mode, 2861 independent reflections ( $R_{int} = 0.0121$ ), 2596 observed reflections [ $I > 2\sigma(I)$ ],  $\mu = 1.898$  mm<sup>-1</sup>,  $T_{min} = 0.549$ ,  $T_{max} = 0.731$ , 122 parameters,  $R_1$  (all data) = 0.0485,  $R_1$  (observed data) = 0.0437, S = GooF = 1.095,  $\Delta$ /s.u. = 0.001, residual  $\rho_{max} = 0.181$  eÅ<sup>-3</sup>.

### Acknowledgments

Financial support from the European Union through contracts HPRN-CT-2000-00010 "Polycat" and G5RD-CT-2001-00554 "Dentalopt" is gratefully acknowledged. We thank Mrs. B. Norberg (Facultés Universitaires de Namur, Belgium) for the XRD analyses and Prof. L. Cavallo (University of Salerno, Italy) for the computations of  $%V_{\rm Bur}$  and a preprint of ref.<sup>[49]</sup>.

- a) A. J. Arduengo III, R. L. Harlow, M. Kline, J. Am. Chem. Soc. 1991, 113, 361–363; b) A. J. Arduengo III, H. V. Rasika Dias, R. L. Harlow, M. Kline, J. Am. Chem. Soc. 1992, 114, 5530–5534; c) A. J. Arduengo III, J. R. Goerlich, R. Krafczyk, W. J. Marshall, Angew. Chem. Int. Ed. 1998, 37, 1963– 1965; d) A. J. Arduengo III, Acc. Chem. Res. 1999, 32, 913– 921.
- [2] For monographs, see: a) G. Bertrand (Ed.), Carbene Chemistry: From Fleeting Intermediates to Powerful Reagents, Marcel Dekker, New York, 2002; b) S. P. Nolan (Ed.), N-Heterocyclic Carbenes in Synthesis, Wiley-VCH, Weinheim, 2006; c) F. Glorius (Ed.), N-Heterocyclic Carbenes in Transition Metal Catalysis, Topics in Organometallic Chemistry, vol. 21, Springer, Berlin, 2007.
- [3] V. Nair, S. Bindu, V. Sreekumar, Angew. Chem. Int. Ed. 2004, 43, 5130–5135.
- [4] D. Enders, O. Niemeier, A. Henseler, *Chem. Rev.* 2007, 107, 5606–5655; N. Marion, S. Díez-González, S. P. Nolan, *Angew. Chem. Int. Ed.* 2007, 46, 2988–3000.
- [5] For reviews, see: a) W. A. Herrmann, C. Köcher, Angew. Chem. Int. Ed. Engl. 1997, 36, 2162–2187; b) L. Jafarpour, S. P. Nolan, Adv. Organomet. Chem. 2001, 46, 181–222; c) W. A. Herrmann, Angew. Chem. Int. Ed. 2002, 41, 1290–1309; d) W. A. Herrmann, T. Weskamp, V. P. W. Böhm, Adv. Organomet. Chem. 2002, 48, 1–69; e) C. M. Crudden, D. P. Allen, Coord. Chem. Rev. 2004, 248, 2247–2273; f) N. M. Scott, S. P. Nolan, Eur. J. Inorg. Chem. 2005, 1815–1828; g) I. Dragutan, V. Dragutan, L. Delaude, A. Demonceau, Arkivoc 2005, 10, 206–253; h) J. C. Garrison, W. J. Youngs, Chem. Rev. 2005, 105, 3978–4008; i) F. E. Hahn, M. C. Jahnke, Angew. Chem. Int. Ed. 2008, 47, 3122– 3172.

- [6] For reviews, see: a) M. C. Perry, K. Burgess, *Tetrahedron:* Asymmetry 2003, 14, 951–961; b) D. Enders, T. Balensiefer, Acc. Chem. Res. 2004, 37, 534–541; c) V. César, S. Bellemin-Laponnaz, L. H. Gade, Chem. Soc. Rev. 2004, 33, 619–636.
- [7] D. Bourrisou, O. Guerret, F. P. Gabbaï, G. Bertrand, Chem. Rev. 2000, 100, 39–91.
- [8] N. Kuhn, A. Al-Sheikh, Coord. Chem. Rev. 2005, 249, 829–857.
- [9] S. Díez-González, S. P. Nolan, Coord. Chem. Rev. 2007, 251, 874–883.
- [10] C. A. Tolman, Chem. Rev. 1977, 77, 313-348.
- [11] a) M. M. Rahman, H. Y. Liu, A. Prock, W. P. Giering, Organometallics 1987, 6, 650–658; b) M. M. Rahman, H. Y. Liu, K. Eriks, A. Prock, W. P. Giering, Organometallics 1989, 8, 1–7; c) D. White, N. J. Coville, Adv. Organomet. Chem. 1994, 36, 95– 158.
- [12] See for example: a) D. C. Woska, M. Wilson, J. Bartholomew, K. Eriks, A. Prock, W. P. Giering, *Organometallics* 1992, 11, 3343–3352; b) A. Demonceau, A. W. Stumpf, E. Saive, A. F. Noels, *Macromolecules* 1997, 30, 3127–3136.
- [13] a) J. Huang, E. D. Stevens, S. P. Nolan, J. L. Petersen, J. Am. Chem. Soc. 1999, 121, 2674–2678; b) J. Huang, H.-J. Schanz, E. D. Stevens, S. P. Nolan, Organometallics 1999, 18, 2370– 2375; c) L. Jafarpour, E. D. Stevens, S. P. Nolan, J. Organomet. Chem. 2000, 606, 49–54; d) J. Huang, L. Jafarpour, A. C. Hillier, E. D. Stevens, S. P. Nolan, Organometallics 2001, 20, 2878– 2882; e) L. Jafarpour, S. P. Nolan, J. Organomet. Chem. 2001, 617–618, 17–27; f) A. C. Hillier, W. J. Sommer, B. S. Yong, J. L. Petersen, L. Cavallo, S. P. Nolan, Organometallics 2003, 22, 4322–4326.
- [14] R. Dorta, E. D. Stevens, N. M. Scott, C. Costabille, L. Cavallo, C. D. Hoff, S. P. Nolan, J. Am. Chem. Soc. 2005, 127, 2485– 2495.
- [15] W. A. Herrmann, J. Schütz, G. D. Frey, E. Herdtweck, Organometallics 2006, 25, 2437–2448.
- [16] L. Mercs, G. N. Labat, A. A. Ehlers, M. Albrecht, Organometallics 2006, 25, 5648–5656.
- [17] A. Fürstner, M. Alcarazo, H. Krause, C. W. Lehmann, J. Am. Chem. Soc. 2007, 129, 12676–12677.
- [18] a) A. R. Chianese, X. Li, M. C. Janzen, J. W. Faller, R. H. Crabtree, *Organometallics* 2003, 22, 1663–1667; b) A. R. Chianese, A. Kovacevic, B. M. Zeglis, J. W. Faller, R. H. Crabtree, *Organometallics* 2004, 23, 2461–2468; c) G. Altenhoff, R. Goddard, C. W. Lehmann, F. Glorius, *J. Am. Chem. Soc.* 2004, 126, 15195–15201; d) S. Leuthäusser, D. Schwarz, H. Plenio, *Chem. Eur. J.* 2007, 13, 7195–7203.
- [19] a) K. Öfele, W.A. Herrmann, D. Mihalios, M. Elison, E. Herdtweck, W. Scherer, J. Mink, J. Organomet. Chem. 1993, 459, 177–184; b) M.-T. Lee, C.-H. Hu, Organometallics 2004, 23, 976–983; c) M. Nonnenmacher, D. Kunz, F. Rominger, T. Oeser, J. Organomet. Chem. 2005, 690, 5647–5653; d) F. E. Hahn, M. Paas, D. Le Van, R. Fröhlich, Chem. Eur. J. 2005, 11, 5080–5085; e) K. E. Krahulic, G. D. Enright, M. Parvez, R. Roesler, J. Am. Chem. Soc. 2005, 127, 4142–4143.
- [20] a) A. Tudose, A. Demonceau, L. Delaude, J. Organomet. Chem. 2006, 691, 5356–5365; b) A. Tudose, L. Delaude, B. André, A. Demonceau, Tetrahedron Lett. 2006, 47, 8529–8533.
- [21] H. A. Duong, T. N. Tekavec, A. M. Arif, J. Louie, Chem. Commun. 2004, 112–113.
- [22] a) A. M. Voutchkova, L. N. Appelhans, A. R. Chianese, R. H. Crabtree, J. Am. Chem. Soc. 2005, 127, 17624–17625; b) A. M. Voutchkova, M. Feliz, E. Clot, O. Eisenstein, R. H. Crabtree, J. Am. Chem. Soc. 2007, 129, 12834–12846.
- [23] a) N. Kuhn, H. Bohnen, G. Henkel, Z. Naturforsch., Teil B
   1994, 49, 1473–1480; b) N. Kuhn, E. Niquet, M. Steimann, I.
   Walker, Z. Naturforsch., Teil B 1999, 54, 1181–1187.
- [24] N. Kuhn, M. Steimann, G. Weyers, Z. Naturforsch., Teil B 1999, 54, 427–433.
- [25] a) L. Jafarpour, A. C. Hillier, S. P. Nolan, *Organometallics* 2002, 21, 442–444; b) M. Alcarazo, S. J. Roseblade, E. Alonso, R. Fernandez, E. Alvarez, F. J. Lahoz, J. M. Lassaletta, J. Am.



*Chem. Soc.* **2004**, *126*, 13242–13243; c) K. Vehlow, S. Maechling, S. Blechert, *Organometallics* **2006**, *25*, 25–28.

- [26] a) S. Lee, J. F. Hartwig, J. Org. Chem. 2001, 66, 3402–3415; b)
  M. S. Viciu, G. A. Grasa, S. P. Nolan, Organometallics 2001, 20, 3607–3612; c) G. A. Grasa, M. S. Viciu, J. Huang, S. P. Nolan, J. Org. Chem. 2001, 66, 7729–7737; d) L. Delaude, M. Szypa, A. Demonceau, A. F. Noels, Adv. Synth. Catal. 2002, 344, 749–756; e) Y. Ma, C. Song, W. Jiang, Q. Wu, Y. Wang, X. Liu, M. B. Andrus, Org. Lett. 2003, 5, 3317–3319; f) O. Navarro, H. Kaur, P. Mahjoor, S. P. Nolan, J. Org. Chem. 2004, 69, 3173–3180.
- [27] a) A. Aidouni, A. Demonceau, L. Delaude, Synlett 2006, 493–495; b) A. Fürstner, M. Alcarazo, V. César, C. W. Lehmann, Chem. Commun. 2006, 2176–2178; c) E. A. Mistryukov, Mendeleev Commun. 2006, 16, 258–259; d) L. Hintermann, Beilstein J. Org. Chem. 2007, 3, 22; e) K. M. Kuhn, R. H. Grubbs, Org. Lett. 2008, 10, 2075–2077; f) A. Aidouni, S. Bendahou, A. Demonceau, L. Delaude, J. Comb. Chem. 2008, 10, 886–892.
- [28] a) H. E. Winberg, D. D. Coffman, J. Am. Chem. Soc. 1965, 87, 2776–2777; b) W. S. Sheldrick, A. Schönberg, E. Singer, P. Eckert, Chem. Ber. 1980, 113, 3605–3609; c) W. Krasuski, D. Nikolaus, M. Regitz, Liebigs Ann. Chem. 1982, 1451–1465.
- [29] G. W. Nyce, S. Csihony, R. M. Waymouth, J. L. Hedrick, *Chem. Eur. J.* 2004, 10, 4073–4079.
- [30] a) R. W. Alder, P. R. Allen, S. J. Williams, J. Chem. Soc., Chem. Commun. 1995, 1267–1268; b) Y.-J. Kim, A. Streitwieser, J. Am. Chem. Soc. 2002, 124, 5757–5761; c) T. L. Amyes, S. T. Diver, J. P. Richard, F. M. Rivas, K. Toth, J. Am. Chem. Soc. 2004, 126, 4366–4374; d) A. M. Magill, K. J. Cavell, B. F. Yates, J. Am. Chem. Soc. 2004, 126, 8717–8724; e) H. Chen, D. R. Justes, R. G. Cooks, Org. Lett. 2005, 7, 3949–3952.
- [31] a) A. W. Hofmann, *Liebigs Ann. Chem. Suppl. 1* 1861, 1–61; b)
   A. W. Hofmann, *Ber. Dtsch. Chem. Ges.* 1880, 13, 1732–1737.
- [32] A. Galindo, D. Miguel, J. Perez, Coord. Chem. Rev. 1999, 193– 195, 643–690.
- [33] a) G. R. Clark, T. J. Collins, S. M. James, W. R. Roper, K. G. Town, J. Chem. Soc., Chem. Commun. 1976, 475–476; b) S. M. Boniface, G. R. Clark, J. Organomet. Chem. 1980, 188, 263– 275.
- [34] P. K. Baker, K. Broadley, N. G. Connelly, J. Chem. Soc., Dalton Trans. 1982, 471–475.
- [35] W. Krasuski, D. Nikolaus, M. Regitz, *Liebigs Ann. Chem.* 1982, 1451–1465.
- [36] J. Nakayama, T. Kitahara, Y. Sugihara, A. Sakamoto, A. Ishii, J. Am. Chem. Soc. 2000, 122, 9120–9126.
- [37] I. S. Butler, J. Svedman, Spectrochim. Acta A 1979, 35, 425– 426.
- [38] K. A. Jensen, P. H. Nielsen, Acta Chem. Scand. 1963, 17, 547– 548.

- [39] a) H. Jacobsen, A. Correa, C. Costabille, L. Cavallo, J. Organomet. Chem. 2006, 691, 4350–4358; b) R. Tonner, G. Heydenrych, G. Frenking, Chem. Asian J. 2007, 2, 1555–1567.
- [40] a) S. Fantasia, J. L. Petersen, H. Jacobsen, L. Cavallo, S. P. Nolan, *Organometallics* 2007, 26, 5580–5889; b) D. M. Khramov, V. M. Lynch, C. W. Bialewski, *Organometallics* 2007, 26, 6042–6049; c) R. A. Kelly III, H. Clavier, S. Giudice, N. M. Scott, E. D. Stevens, J. Bordner, I. Samardjiev, C. D. Hoff, L. Cavallo, S. P. Nolan, *Organometallics* 2008, 27, 202–210.
- [41] a) F. Ibáñez, J. G. Santos, J. Chem. Soc. Perkin Trans. 2 1984, 1323–1326; b) T. Campino, J. G. Santos, F. Ibáñez, J. Chem. Soc. Perkin Trans. 2 1986, 1021–1024.
- [42] J. D. Holbrey, W. M. Reichert, I. Tkatchenko, E. Bouajila, O. Walter, I. Tommasi, R. D. Rogers, *Chem. Commun.* 2003, 28–29.
- [43] J. J. Vittal, P. A. W. Dean, Acta Crystallogr., Sect. C 1997, 53, 1879–1881.
- [44] F. H. Allen, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor in *International Tables for Crystallography* (Ed.: E. Prince), Springer, Berlin, **2006**, vol. C, pp. 790–811.
- [45] a) M. L. Ziegler, H. Weber, B. Nuber, O. Serhadle, Z. Naturforsch., Teil B 1987, 42, 1411–1418; b) A. Nagasawa, I. Akiyama, S. Mashima, J. Nakayama, *Heteroat. Chem.* 1995, 6, 45–49; c) T. Fujihara, T. Ohba, A. Nagasawa, J. Nakayama, K. Yoza, Acta Crystallogr., Sect. C 2002, 58, 0558–0559.
- [46] a) L. L. Borer, J. V. Kong, D. E. Oram, *Acta Crystallogr., Sect.* C 1989, 45, 1169–1170; b) M. Akkurt, S. Öztürk, H. Küçükbay, E. Orhan, O. Büyülgüngör, *Acta Crystallogr., Sect. E* 2004, 60, 0219–0221.
- [47] L. Cavallo, A. Correa, C. Costabille, H. Jacobsen, J. Organomet. Chem. 2005, 690, 5407–5413.
- [48] A. Poater, F. Ragone, S. Giudice, C. Costabile, R. Dorta, S. P. Nolan, L. Cavallo, *Organometallics* 2008, 27, 2679–2681.
- [49] A. Poater, B. Cosenza, A. Correa, S. Giudice, F. Ragone, V. Scarano, L. Cavallo, *Eur. J. Inorg. Chem.* 2009, 1759–1766; this issue.
- [50] a) A. Fürstner, L. Ackermann, B. Gabor, R. Goddard, C. W. Lehmann, R. Mynott, F. Stelzer, O. R. Thiel, *Chem. Eur. J.* 2001, 7, 3236–3253; b) M. Barbasiewicz, M. Bieniek, A. Michrowska, A. Szadkowska, A. Makal, K. Wozniak, K. Grela, *Adv. Synth. Catal.* 2007, 349, 193–203.
- [51] W. A. Herrmann, C. Köcher, L. J. Goossen, G. R. J. Artus, *Chem. Eur. J.* **1996**, *2*, 1627–1636.
- [52] A. J. Arduengo III, R. Krafczyk, R. Schmutzler, H. A. Craig, J. R. Goerlich, W. J. Marshall, M. Unverzagt, *Tetrahedron* 1999, 55, 14523–14534.
- [53] K. Issleib, A. Brack, Z. Anorg. Allg. Chem. 1954, 277, 258-270.
- [54] G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.
- [55] A. L. Speck, *PLATON*, A Multipurpose Crystallographic Tool, Utrecht University, The Netherlands, 2005.

Received: November 13, 2008 Published Online: February 17, 2009