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Synthesis and Electronic Structure of Carbene Complexes Based on a Sulfonyl-Substituted Dilithio Methandiide

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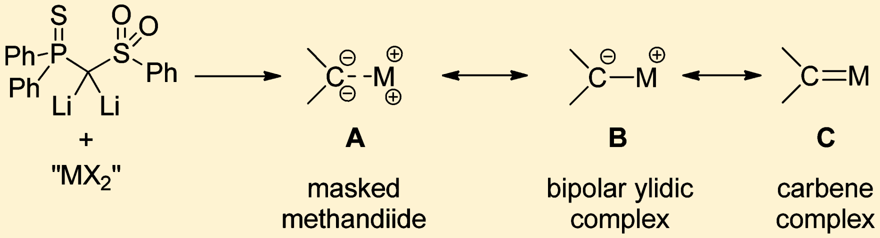
Supporting Information



ABSTRACT: The application of a sulfonyl-substituted dilithio methandiide in the synthesis of carbene complexes was examined. In all cases, the metal carbon interaction was found to be highly polar with only small π-contribution. Hence, the stability of these complexes was found to greatly rely on the coordination ability of the side-arms supporting the metal carbon interaction. As such, the sulfonyl moiety allowed the isolation of a carbene complex with the oxophilic zirconium, which is the first of its kind bearing no (bis)phosphonium ligand framework. On the contrary, complexes with the late transition metals ruthenium and palladium were found to be more labile due to the facile decoordination of the sulfonyl moiety. This results in the opening of a reactive coordination site at the metal center and hence in further reactions such as cyclometalation or sulfur transfer from the thiophosphoryl moiety to the carbenic carbon atom.

INTRODUCTION

Transition metal complexes with a metal carbon double bond have found wide-ranging applications in various catalytic and stoichiometric transformations.[1] The reactivity of these compounds was found to be strongly influenced by the substituents bound to the carbenic carbon atom, thus leading to their classification as Fischer-type carbene and Schrock-type alkylidene complexes.[2] However, in recent years carbene complexes derived from geminal dilithiated compounds have gained special interest, as they seem to contradict this general classification pattern.[3] Here, the metal carbon bond is formally formed by a four-electron donation from the ligand to the metal.[4] Yet, the bonding situation in these systems was found to vary strongly depending on the nature of the metal and its coligands. Thus, the metal carbon interaction in these complexes covers a range of bonding situations, starting from a kind of masked methandiide with mainly electrostatic $M^{2+}\cdots C^{2-}$ interactions (**A**), to ylidic complexes with a carbanionic ligand, $M^+{-}C^-$ (**B**), and complexes with a real M═C double bond (**C**) (Figure 1).[5] These flexible bonding properties allowed the isolation of a series of carbene complexes incorporating early and late transition metals, but also lanthanides and actinides.[6]

However, systematic studies on the bonding situation are strongly restricted, due to the limited number of dianionic starting compounds.[7] In particular, the impact of the α-substituents at the carbenic carbon atom on the metal carbon bond and the complex stability is virtually unexplored. So far, bis(phosphonium)-stabilized dianions, above all bis(thiophosphoryl) and bis(iminophosphoryl) methandiides, have been the only dianionic ligand systems applied in this carbene chemistry. Supported by the pincer-type coordination mode, these methandiides allowed the isolation of quite unusual carbene-like complexes with metals in various oxidation states as reported by the groups of Cavell, Liddle, Le Floch, Mézailles, Harder, and others. Among others are the first cerium(IV)−carbon multiple bond,[8] uranium-carbene complexes with various oxidation states of the metal center,[9] main group metal carbene-like complexes,[10] or nucleophilic carbene complexes with late transition metals.[11]

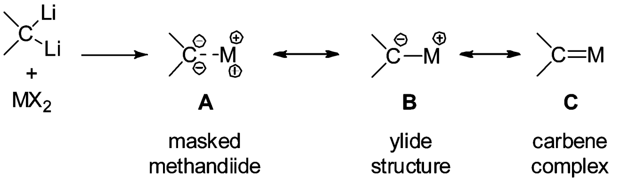


Figure 1. Bonding situations in carbene complexes based on dilithio methandiides.

In order to explore the generality of this carbene chemistry and an extension to other methandiide ligands in order to study the influence of the substituents at the central carbon atom on the nature of the metal carbon bond, our group has aimed at the development of novel dilithio methandiides.[12] Recently, we

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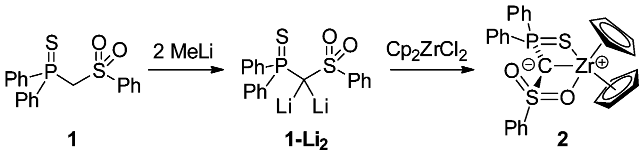
reported on the clean and high-yielding dilithiation of the sulfonyl-substituted precursor **1**. The stabilized methandiide **1-Li$_2$** was found to exhibit unique structural and electronic properties reflecting the strong anion-stabilizing ability of both the thiophosphoryl and the sulfonyl substituent.[13] Thus, this dianion seemed to be an ideal candidate for the transfer to transition metals. We were particularly interested in whether the sulfonyl substituent would change the properties of the metal carbon bond and whether the different coordination ability of the sulfonyl moiety would also influence the reactivity of the metal complexes. Here, we report the synthesis of transition metal carbene complexes and how the sulfonyl substituent influences the ligand metal interaction and the complex stability.

RESULTS

Synthesis and Stability of the Carbene Complexes. In order to compare the bonding properties of our new ligand systems, we first aimed at the synthesis of complexes comparable to compounds with the related bis(thiophosphoryl) methandiide ligand. Thereby, we chose zirconium as early and ruthenium and palladium as late transition metals. The synthesis of the zirconium carbene complex was accomplished by treatment of dianion **1-Li$_2$** with an equivalent amount of zirconocene dichloride in toluene. For an improved synthetic procedure for dianion **1-Li$_2$** from **1** see the Supporting Information (SI). ^{31}P{^{1}H} NMR spectroscopy of the crude product revealed quantitative formation of a single new species with upfield shifted resonance (δ_P = 17.6 ppm) compared to the starting compound (δ_P = 26.2 ppm). After removal of the formed lithium chloride the product was isolated as a yellow solid in 63% yield. **2** represents the first example of a carbene complex derived from a methandiide ligand with a substituent other than a phosphonium group. **2** was characterized by multinuclear NMR spectroscopy and elemental and single-crystal X-ray diffraction analysis. The ^{13}C{^{1}H} NMR resonance of the carbene carbon atom appears as a doublet at 41.0 ppm with a coupling constant of $^1J_{PC}$ = 107.6 Hz. This resonance is slightly downfield shifted compared with the bis(thiophosphoryl)-substituted analogue, but considerably upfield shifted compared to signals reported for other zirconium carbene complexes.[15,16] This indicates incomplete charge transfer from the carbon to the metal and a distinct negative charge remaining at the carbenic carbon atom. The large $^1J_{PC}$ coupling constant accounts for a high s-character of the carbon atom.

Scheme 1. Synthesis of Zirconium Carbene Complex 2 from Methandiide 1-Li$_2$



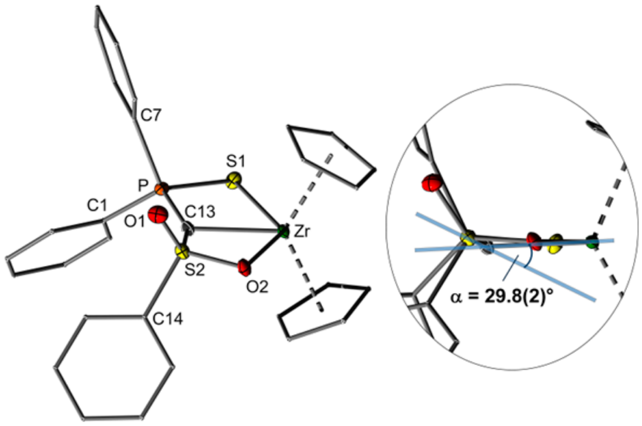
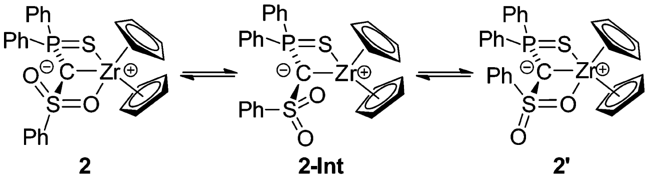


Figure 2. (Left) Molecular structure of complex **2**. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms and solvent molecule are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Zr–C13 2.2419(18), Zr–O2 2.3019(14), Zr–S1 2.7609(5), S2–O1 1.4507(14), S2–O2 1.5128(14), S2–C13 1.609(2), S2–C14 1.780(2), S1–P 2.0226(7), P–C13 1.673(2), P–C7 1.8169(19), P–C1 1.818(2); S2–C13–P 149.66(12), S2–C13–Zr 97.77(9), P–C13–Zr 108.48(9). (Right) Extract of the molecular structure showing the geometry of the carbene carbon atom.

Single crystals for X-ray diffraction analysis of **2** were grown by cooling of a diethyl ether solution to −30 °C. **2** crystallizes in the non-centrosymmetric orthorhombic space group $Pna2_1$ with an additional diethyl ether molecule (not depicted in Figure 2). The molecular structure clearly confirms the 3-fold coordination of the central carbon atom with a C–Zr distance of 2.232(2) Å. This bond length is in the range of zirconium carbene complexes based on bis(phosphonium) methandiides (e.g., 2.251 Å for LZrCp$_2$ or 2.172 Å for LZrCl$_2$Py$_2$ with L = C[P(S)Ph$_2$]$_2$),[14] but slightly shorter than those found in NHC complexes (2.35–2.47 Å)[15] and longer than those in alkylidene complexes (2.00–2.10 Å).[16] The most remarkable feature of the molecular structure of **2**, however, concerns the geometry of the carbene moiety. **2** features a tilt between the planes of the P–C13–S2 and the C–Zr–S1–O2 moiety by 29.8(2)° [dihedral P–C13–S–Zr: 25.1(1)°] and thus a slightly pyramidalized carbon atom. Similar distortions have been reported for some of the bis(phosphonium)-substituted complexes.[17] It is also interesting to note that the C–P (1.673(2) Å) and C–S (1.609(2) Å) distances in the zirconocene complex are shorter than those found for dilithio methandiide **1-Li$_2$** and thus shortened by approximately 10% compared to the neutral ligand **1**.[13] This shortening is the result of electrostatic interactions within the P–C–S backbone and thus indicative for a still present charge accumulation at the central carbon atom. This is in line with the ^{13}C{^{1}H} NMR signal of the carbenic carbon atom observed at remarkable high field. Analogously, due to negative hyperconjugation effects, bond lengthening is observed for all other bonds to phosphorus and sulfur (S2), respectively.

Overall, the methandiide ligand **1** coordinates in a pincer-type coordination mode via both the thiophosphoryl and the sulfonyl moiety. The coordination of only one oxygen of the sulfonyl moiety and the pyramidalization of the carbon atom leads to the formation of diastereomers, whereas only the R_CR_S diastereomer is found in the crystal. In solution however, a fluxional behavior is observed. At 21 °C, the ^{1}H NMR spectrum shows only a single somewhat broadened resonance at δ = 6.11 ppm for the cyclopentadienyl moieties as well as broadened signals in the aromatic region. This suggests fluxional behavior of the sulfonyl moiety at room temperature with a rapid interconversion between the two coordination modes **2** and **2′** (Scheme 2). ^{1}H NMR spectroscopy in CD$_2$Cl$_2$ was used to study this isomerization process and to determine the corresponding activation parameters (see the SI). Cooling the

Scheme 2. Fluxional Behavior of 2



sample to −80 °C first results in a broadening of the signals and finally in two, well-resolved Cp resonances as well as a splitting of the signals for the Ph groups of the Ph_2PS moiety. Coalescence was observed at $T_c = -26$ °C ($\delta = 6.10$; fwhw = 49 Hz), thus allowing for an estimation of the free energy of the activation barrier for the rotation process by applying the Eyring equation ($\Delta G^{\ddagger} = 52$ kJ mol^{-1}).

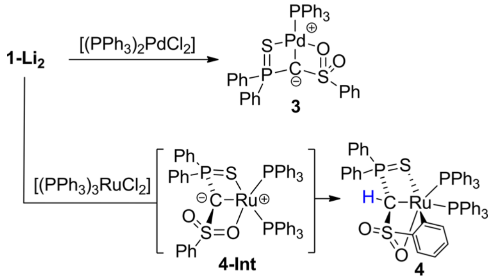
To further analyze this behavior and the different isomers of **2**, DFT studies were performed on the real system employing the B3LYP functional in combination with the LANL2TZ(f) basis set for Zr and the 6-311+G(d,p) for all other atoms. The energy-optimized structure is in excellent agreement with the molecular structure of **2** [Zr–C: 2.248 Å (calcd), 2.242(2) Å (expt); P–C–S: 146.0° (calcd) 149.7(2)° (expt)] with the bending of the carbene moiety being also well reproduced by the calculations (dihedral C13–P–S–Zr: 24.7° (calcd) 25.1(1) (expt)). The calculations showed no minimum for the R_CS_S isomer. Energy optimization always gave the R_CR_S and S_CS_S isomer, respectively. A planar carbene structure, however, was found to be only slightly disfavored, by 4.6 kJ·mol^{-1}, confirming the pyramidalization observed in the molecular structure. The rotation about the C–S bond—to alter the coordination between the two sulfonyl oxygen atoms and thus the configuration of the sulfur atom—was found to require 72.8 kJ·mol^{-1}, a barrier higher than the one derived from the VT-NMR experiments. However including solvent effects through a polarizable continuum model (solvent = DCM) gave an activation energy of 53.4 kJ·mol^{-1}, which is in good agreement with the experiment. This value additionally confirms the fluxional coordination behavior in solution at room temperature.

Zirconocene complex **2** turned out to be unreactive toward several organic substrates (benzophenone, iodomethane, silanes, disulfides, alkynes). Even at elevated temperatures and in different solvents (toluene, thf) no conversion was observed (see SI). Yet, **2** is highly moisture-sensitive and readily abstracts protons from the solvent or protic reagents such as aldehydes. This repeatedly lead to a complete break of the metal carbon bond and the re-formation of the protonated ligand **1**, thus accounting for a weak metal ligand interaction.

In the next step we addressed the synthesis of carbene complexes with the late transition metals ruthenium and palladium. Treatment of methandiide **1** with $[(PPh_3)_2PdCl_2]$ showed no clean formation of a single product. Yet, the main product, which is characterized by two doublets in the $^{31}P\{^1H\}$ NMR spectrum resonating at $\delta_P = 17.9$ and 39.9 ppm ($^3J_{PP} = 38.7$ Hz), was identified as the expected carbene complex **3**. This complex was found to be also accessible via an alternative route using a carbenoid analogue of **1**, $[Ph_2PS(SO_2Ph)C(Cl)\text{-}Li]$, and the Pd(0) precursor $[Pd(PPh_3)_4]$.[18,19] However, **3** is not stable at room temperature in solution and decomposed in the course of the workup procedure to form protonated species as well as a thioketone complex by sulfur transfer from the phosphorus to the carbenic carbon atom. This instability of complex **3** can probably be referred to the weak coordination ability of the sulfonyl moiety. For the related bis(phosphonium)-substituted carbene complex no decomposition was reported.[11]

Treatment of equimolar amounts of dilithio methandiide **1** with $[(PPh_3)_3RuCl_2]$ in toluene at room temperature instantly results in the darkening of the reaction mixture. NMR studies of the crude product revealed the formation of triphenyl phosphine together with a single new compound, which was isolated as an orange solid in 62% yield (Scheme 3). Isolation and crystallization revealed the formation of the cyclometalation product **4**. Thereby, the metalation was found to selectively occur at the phenyl ring of the sulfonyl moiety. Compound **4** was characterized by multinuclear NMR as well as elemental and single-crystal X-ray diffraction analysis. The $^{31}P\{^1H\}$ NMR spectrum features three signals of equal intensity at 45.5 (dd), 55.3 (d), and 68.1 (d) ppm, whereas only the phosphorus (P3, Figure 3) of the PPh_3 ligand in *trans* position to the central carbon atom is involved in coupling to both other phosphorus nuclei. The proton at the metalated carbon (C13) was found as a multiplet at 2.88 ppm in the ^1H NMR spectrum.

Scheme 3. Synthesis of Palladium and Ruthenium Complexes 3 and 4



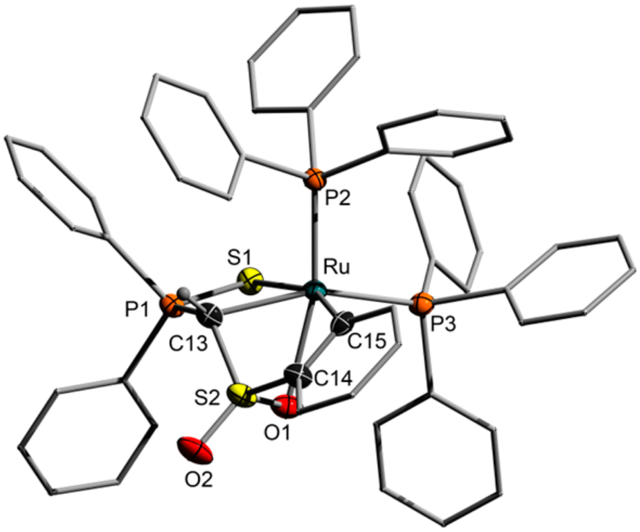


Figure 3. (Left) Molecular structure of complex **4**. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms and solvent molecule are omitted for clarity. Selected bond lengths [Å] and angles [deg]: C13–S2 1.724(6), C13–P1 1.779(6), C13–Ru 2.191(6), C15–Ru 2.070(6), O1–S2 1.483(4), O1–Ru 2.332(4), O2–S2 1.443(4), P1–S1 1.998(2), P2–Ru 2.2668(16), P3–Ru 2.3731(17), Ru–S1 2.5558(17), S2–C13–P1 116.6(3).

Single crystals of **4** were obtained by diffusion of diethyl ether into a saturated dichloromethane solution. The Ru complex crystallizes in the monoclinic space group $P2_1/c$. The ruthenium center is 6-fold coordinated, strongly deviating from the ideal octahedral geometry. Thereby, the sulfonyl ligand acts as a tetradentate ligand binding in a *S,C,C,O*-coordination mode. Due to the coordination of only one oxygen of the sulfonyl moiety (O1), two pairs of diastereomers are formed. However, the cyclometalation was found to be diastereoselective, solely producing the ($R_C S_S$) and ($S_C R_S$) couple.

An analogous cyclometalation reaction was reported by Le Floch, Mézailles, and co-workers with bis(phosphonium)-substituted dianions.[20] Yet, in the case of the symmetric bis(thiophosphoryl) methandiide the isolation of the intermediate carbene complex was possible and cyclometalation occurred only at 120 °C. In the case of the sulfonyl-substituted methandiide the cyclometalation was found to be extremely fast at room temperature, being complete after only a couple of minutes after mixing of the starting materials. Attempts to trap the intermediate carbene species **4-int**—such as with aldehydes—even at low temperatures (−78 °C) always gave way to the clean formation of **4**, indicating a low reaction barrier.

The mechanism of the cyclometalation of the bis(phosphonium) ligand was reported to be a stepwise process starting with a C−H bond activation at the ruthenium center and followed by H-shift from the ruthenium to the central carbon atom.[20] Thereby, the rate-determining step for the cyclometalation was found to be the decoordination of one of the thiophosphoryl moieties prior to the C−H activation step. The fact that the sulfonyl complex **4-int** undergoes cyclometalation even at −78 °C suggests that the weaker coordination ability of the sulfonyl side-arm might be the reason for the fast process. In order to rationalize this mechanism also for the formation of **4**, DFT studies employing the B3LYP functional in combination with the 6-31++G(d,p) (for all nonmetal atoms) and the LANL2TZ(f) basis set (for Ru) were performed using a model system with PMe_3 ligands instead of PPh_3. The calculations revealed an analogous stepwise mechanism to the cyclometalation product **4** (for a display of the whole reaction process, see the SI). An alternative direct *ortho*-metalation via deprotonation of the phenyl group by the nucleophilic carbene carbon atom showed a considerably higher reaction barrier of 148.8 kJ·mol^{-1} compared to only 46.8 kJ·mol^{-1} (**TS1**, Figure 4) for the stepwise reaction pathway. Hereby, the decoordination and rotation of the sulfonyl moiety to allow for the proximity between the ruthenium center and the phenyl substituent turned out to be the rate-determining step. The remarkably low activation barrier of 46.8 kJ·mol^{-1} (**TS1**) corroborates with the failed attempts to isolate the intermediate carbene complex **4-int** and with the fast reaction process.

The computational studies also reflect the observed selectivities of the cyclometalation (Figure 4). The alternative metalation of one of the phosphorus-bound phenyl substituents showed a clearly higher reaction barrier of 117.4 kJ·mol^{-1} (**TS1′**) compared to the sulfonyl moiety (cf. 46.8 kJ·mol^{-1} to **4**). Again, the rate-determining step is the rotation of the thiophosphoryl moiety. These findings demonstrate that the selective metalation of the sulfonyl phenyl substituent is due to the different coordination abilities of the sulfonyl group compared with the thiophosphoryl moiety. Even prolonged heating of complex **4** in C_6D_6 did not result in any clear transformation to further cyclometalation products, but in the decomposition to multiple products. Also, the ($S_C S_S$) and ($R_C R_S$) diastereomer of **4** was revealed to be thermodynamically disfavored over the isomers found in the crystal ($\Delta\Delta G$ = 87.7 kJ·mol^{-1}). Overall, the calculations explain the thermal lability of **4-int** and the selective formation of complex **4**.

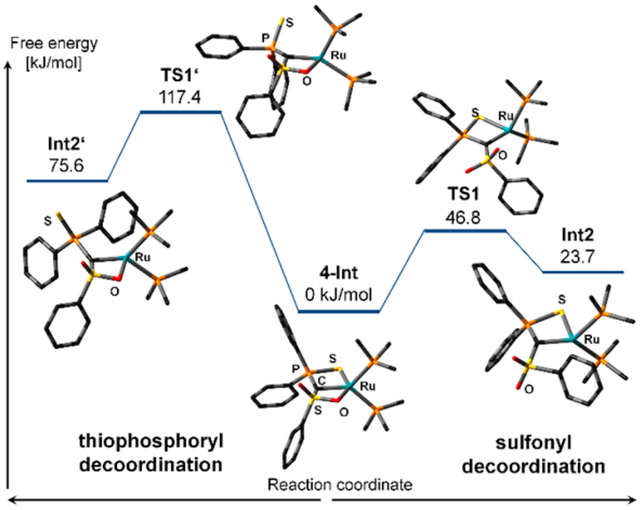


Figure 4. Comparison of the energies for the activation of the sulfonyl- and thiophosphoryl-bound phenyl substituent.

Computational Studies on the Metal Ligand Interaction. The experimental studies of the three carbene complexes **2**, **3**, and **4-int** account for a weak ligand metal interaction with the novel methandiide **1-Li$_2$**. To further explore the electronic structure and the nature of the metal carbon bonds, DFT studies were performed. Due to computational costs, the PPh_3 ligands in the two phosphine complexes were replaced by PMe_3. Figure 5 depicts the atomic charges obtained from the NBO analysis[21] as well as the Wiberg bond indices for the metal ligand interactions. In all three carbene complexes high negative charges are observed for the central carbon atoms, thus reflecting the high nucleophilicity of these complexes. Thereby, the highest negative charge (q_C = −1.42) is observed for the zirconium complex **2**. This, together with the positive charge at zirconium (q_{Zr} = 1.35), accounts for a considerable ionic nature of the metal carbon interaction. These findings corroborate with the spectroscopic observations (^{13}C NMR shift, C−P/S bond shortening). The same holds true for the ruthenium and palladium complexes. Yet, in these cases the metal centers are more electron-rich.

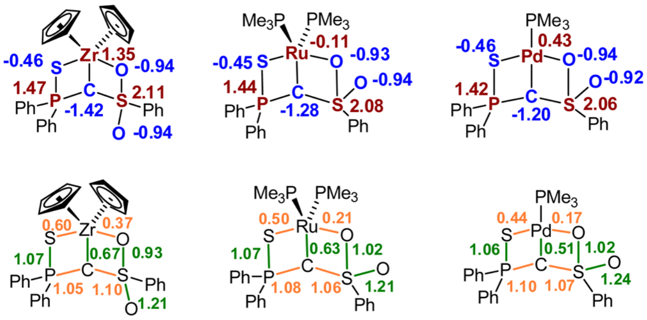


Figure 5. Natural atomic charges (top) and Wiberg bond indices of the carbene complexes.

Ionic interactions play also an important role for the stabilization of the negative charge within the ligand backbone. The charges in the sulfonyl and thiophosphoryl moieties are almost independent of the metal center. The positive charges at the phosphorus and sulfur atoms are comparable to the charges observed for the parent methandiide **1**-**Li**$_2$ and thus emphasize the importance of electrostatic interactions also for the stabilization of these carbene complexes.

These findings are further manifested by the NBO analyses and Wiberg bond indices (WBI) of the complexes. In the case of zirconium complex **2** a WBI of only 0.674 as well as a high polarization of the Zr−C bond toward the carbon end was found. This is true for both the σ- and π-interaction of the metal carbon bond, as evidenced by the molecular and natural bond orbitals. The latter features high orbital coefficients (0.89 ≙ 79.7% and 0.95 ≙ 90.0%) at the carbon atom (Figure 6).[22] In the case of the ruthenium and palladium complexes even lower bond indices are observed for the M−C bond at that level of theory. Additionally, the NBO analyses revealed only a σ-interaction and a remaining lone pair at the central carbon atom. Overall, the methandiide-based carbene complexes reported herein feature only weak π-interactions. The metal carbon bond is thus best described by means of the bipolar ylidic resonance structure **B** with little contribution of the carbene structure **C** (Figure 1). Hence, the zirconium complex **2** can be viewed as an 18 valence electron complex (cf. Scheme 1) and not as a 20-electron species, as implied by a carbene-type description.[14b] This is well in line with the observed stability of **2**.

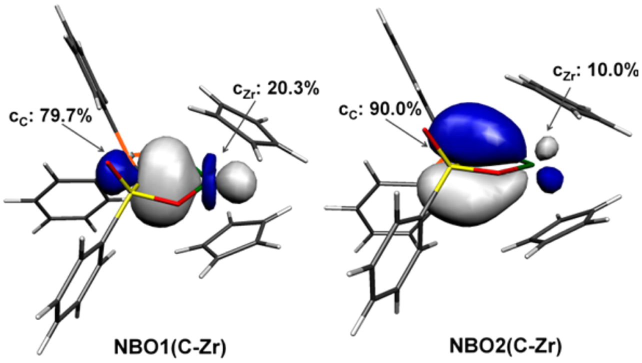


Figure 6. NBO plot with the corresponding σ- and π-interactions of the C−Zr bond (isosurface value 0.03).

These metal carbon interactions are comparable to related bis(phosphonium)-substituted systems, in which the strong anion-stabilizing ability of the phosphonium groups stabilizes polarized M−C bonds. As such, a WBI(Zr−C) of 0.67 and a negative charge at the central carbon atom of $q_C = -1.53$ have also been reported for a zirconocene complex analogous to **2**.[6a] Yet, the stability of the sulfonyl-substituted complexes was found to be considerably lower. Judging from the results of the NBO analysis, this increased lability cannot be referred to changes in the electronic situation of the M−C bond. The observations made in experiment, however, suggested that the weaker coordination ability of the sulfonyl moiety compared with a phosphonium group might be the origin of the different stabilities. This is also supported by the WBIs of the related M−O interactions (see Figure 5). These values are in all cases considerably smaller than those found for the M−S interaction with the thiophosphoryl moiety. For example, for the ruthenium complex **4-int** the bond index of the M−O bond (WBI = 0.21) is less than half of the value calculated for the M−S bond (0.50). These low bond indices are in line with the fluxional behavior observed for zirconium complex **2** in solution and the selective C−H activation of the phenyl substituent of the sulfonyl moiety. Also, for all complexes isomers without additional coordination of the sulfonyl moiety were found to be only slightly disfavored over the pincer-type coordination mode. For example in the case of the ruthenium complex **4-int** a destabilization by only 23.7 kJ·mol^{-1}, and for the palladium complex **3** by only 17.2 kJ·mol^{-1}, is calculated.

Overall the metal carbon interactions in the presented carbene complexes based on the sulfonyl-substituted methandiide **1**-**Li**$_2$ are comparable to those reported for the widely applied bis(phosphonium)-substituted systems. Yet, the weaker coordination ability of the sulfonyl moiety crucially affects the stability and thus the reactivity of the complexes. However, the use of more electron-deficient metal centers should allow the isolation of further carbene complexes based on **1**. Here the flexible coordination ability of the sulfonyl moiety should allow for the approach, coordination, and activation of various organic substrates.

■ CONCLUSIONS

In conclusion, we presented the first examples of carbene complexes based on a non-bis(phosphonium)-substituted methandiide. The reactivity and stability of these complexes showed that the pincer-type coordination mode is crucial for the stabilization of this unique type of carbene species. While the metal carbon interactions were found to be comparable to those in the bis(phosphonium)-based ligand systems (i.e., highly polar M−C interactions with small π-contribution), the weaker coordination ability of the sulfonyl moiety limits the stability of these complexes. These findings clearly show that the coordination of additional side-arms is crucial to support the metal carbon interaction in these carbene complexes and to stabilize the unusual bonding situation. In the case of our newly developed methandiide ligand **1**-**Li**$_2$ the weak coordination ability of the sulfonyl moiety so far only allowed the isolation of a zirconium carbene complex in good yields due to the oxophilic nature of the metal. For ruthenium and palladium the stabilization was found to be insufficient, resulting in further reactions such as cyclometalation or sulfur transfer from the thiophosphoryl moiety to the carbenic carbon atom.

These results demonstrate that also methandiides with substituents other than phosphonium groups can be applied for the synthesis of carbene complexes. By increasing the ligand−metal charge transfer and thus the π-interaction of the M−C bond, more stable carbene complexes should be accessible. Yet, the flexible coordination behavior of substituents such as the sulfonyl moiety may allow for the creation of open coordination sites at the metal center. This should allow for a rich chemistry toward organic substrates and the possibility for bond activation reactions with the participation of the ligand framework.

■ EXPERIMENTAL SECTION

General Procedure. All experiments were carried out under a dry, oxygen-free argon atmosphere using standard Schlenk techniques. Involved solvents were dried over sodium or potassium (or over P_4O_{10}, CH_2Cl_2) and distilled prior to use. H_2O is distilled water. Organolithium reagents were titrated against diphenylacetic acid prior to use. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on Avance-500, Avance-400, or Avance-300 spectrometers at 22 °C if not stated otherwise. All values of the chemical shift are in ppm regarding the δ-scale. All spin−spin coupling constants (J) are given in hertz (Hz). To display multiplicities and signal forms correctly, the following abbreviations were used: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad signal. Signal assignment was supported by DEPT and HMQC experiments. Elemental analyses were performed on an Elementar Vario MICRO-cube elemental analyzer. All reagents were purchased from Sigma-Aldrich, ABCR, Rockwood Lithium, or Acros Organics and used without further purification. For an improved synthetic procedure for ligand **1**, see the SI.

Synthesis of 1-Li$_2$. To a solution of 350 mg (0.94 mmol) of sulfon **1** in 20 mL of dry THF at 0 °C was added 0.41 mL (2.07 mmol) of methyllithium (1.46 M in diethyl ether). The mixture was stirred at room temperature for 1 h, followed by a reduction of the solvent *in vacuo* to about 10 mL. The resulting yellow reaction mixture was stirred for an additional 20 h, whereupon a colorless precipitate was formed. The solid was washed with pentane and dried *in vacuo* (396 mg, 0.80 mmol, 86%). The NMR data of the dilithiated compound agree with the published ^{1}H and ^{31}P{^{1}H} NMR spectra.[13]

Synthesis of Complex 2. A solution of 150 mg (0.30 mmol) of methandiide **1-Li$_2$** was added dropwise to a suspension of 88.9 mg (0.30 mmol) of Cp_2ZrCl_2 in 5 mL of dry toluene. The pale yellow reaction mixture was stirred for 17 h at room temperature, upon which an intense yellow suspension formed. After filtration the solvent was removed *in vacuo*, affording a solid residue. The solid was taken up in a minimum amount of diethyl ether and cooled to −30 °C, thus affording the diethyl ether solvate of **2** as a pale yellow, crystalline solid (127 mg, 0.19 mmol, 63%). ^{1}H NMR (500.1 MHz, CD_2Cl_2): δ 1.15 (t, $^3J_{HH}$ = 7.00 Hz, 6 H; CH_3-Et_2O), 3.43 (q, $^3J_{HH}$ = 6.94 Hz, 4 H; CH_2-Et_2O), 6.11 (s, CH_{Cp}), 7.25 (t, $^3J_{HH}$ = 7.53 Hz, 2 H; $CH_{PPh,para}$), 7.38 (t, $^3J_{HH}$ = 7.35 Hz, 1 H; $CH_{SPh,para}$), 7.46−7.55 (m, 8 H; $CH_{PPh,meta}$, $CH_{SPh,ortho,meta}$), 7.80 (br, 4 H; $CH_{PPh,ortho}$). ^{13}C NMR (125.8 MHz, CD_2Cl_2): δ 15.5 (CH_3-Et_2O), 41.0 (d, $^1J_{PC}$ = 108.6 Hz; PCS), 66.1 (CH_2-Et_2O), 113.5 (CH_{Cp}), 124.6 (CH_{SPh}), 128.8 (d, $^3J_{PC}$ = 12.7 Hz; $CH_{PPh,meta}$), 129.0 (CH_{SPh}), 130.8 (d, $^2J_{PC}$ = 12.8 Hz; $C_{PPh,ortho}$), 131.1 ($CH_{SPh,para}$), 131.5 (d, $^4J_{PC}$ = 3.13 Hz; $C_{PPh,para}$), 137.2 (d, $^1J_{PC}$ = 79.1 Hz; $C_{PPh,ipso}$), 148.4 ($C_{SPh,ipso}$). ^{31}P{H} NMR (202.5 MHz, CD_2Cl_2): δ 17.5. Anal. Calcd for $C_{33}H_{35}O_3PS_2Zr$: C, 59.51; H, 5.29; S, 9.63. Found: C, 59.46; H, 5.44; S, 9.26.

Synthesis of Complex 3. A 74.0 mg (0.15 mmol) amount of methandiide **1-Li$_2$** and 105 mg (0.15 mmol) of $PdCl_2(PPh_3)_2$ were dissolved in 10 mL of dry toluene, and the red-orange reaction mixture was stirred overnight at room temperature. After this time, ^{31}P{^{1}H} NMR of the reaction mixture showed complete conversion of the reactants. The solvent was evaporated *in vacuo*, and the orange residue was washed three times with *n*-pentane and cold diethyl ether, leaving an orange solid (57.7 mg, 0.08 mmol, 52%). For spectroscopic data see ref 18.

Synthesis of Complex 4. A 137 mg (0.14 mmol) portion of $(PPh_3)_3RuCl_2$ was suspended in 4 mL of dry toluene, and a solution of 70.9 mg (0.14 mmol) of dianion **1-Li$_2$** in 5 mL of dry toluene was added at room temperature. After stirring of the dark brown reaction mixture for 24 h, the solution was separated from the formed precipate via filtration. The solvent was evaporated *in vacuo*, and the dark brown crude product was purified by washing with dry diethyl ether (3 × 7 mL), yielding the product as a light orange solid (88.7 mg, 0.09 mmol, 62%). Crystals of **4** were obtained by diffusion of diethyl ether into a saturated dichloromethane solution. ^{1}H NMR (300.1 MHz, CD_2Cl_2): δ 2.86−2.90 (ddd, $^2J_{PH}$ = 5.89 Hz, $^3J_{PH}$ = 3.72 Hz, $^3J_{PH}$ = 1.85 Hz, 1 H; PCHS), 5.89 (dt, $^3J_{HH}$ = 7.72, $^4J_{HH}$ = 0.48 Hz, 1 H; $CH_{SPh,H-5}$), 6.42 (td, $^3J_{HH}$ = 7.47, $^4J_{HH}$ = 1.53 Hz, 1 H; $CH_{SPh,H-4}$), 6.66−6.73 (m, 6 H; $CH_{PPh3,ortho}$), 6.80 (td, $^3J_{HH}$ = 7.36 Hz, $^4J_{HH}$ = 0.80 Hz, 1 H; $CH_{SPh,H-3}$), 6.93−6.98 (m, 6 H; $CH_{PPh3,meta}$), 7.09−7.14 (m, 6 H; $CH_{PPh3,meta}$), 7.21−7.48 (m, 21 H; $CH_{PPh3,ortho,para}$, $CH_{SPh,H-2}$, $CH_{PPh,ortho,meta,para}$), 7.70−7.78 (m, 2 H, $CH_{PPh,ortho}$). ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2): δ 37.7 (br, PCS), 125.5 (CH_{SPh-C3}), 124.9 (CH_{SPh-C2}), 127.0 (CH_{SPh-C4}), 127.1 (d, $^1J_{CP}$ = 220.5 Hz; $C_{PPh,ipso}$), 127.6 (d, $^3J_{CP}$ = 4.63 Hz; $CH_{Ru-PPh,meta}$), 127.7 (d, $^3J_{CP}$ = 4.63 Hz; $CH_{Ru-PPh,meta}$), 128.4 (d, $^3J_{CP}$ = 12.3 Hz; $CH_{PPh,meta}$), 129.1 (d, $^4J_{CP}$ = 2.42 Hz; $CH_{Ru-PPh,para}$), 129.2 (d, $^4J_{CP}$ = 2.42 Hz; $CH_{Ru-PPh,para}$), 130.6 (d, $^2J_{CP}$ = 10.5 Hz; $CH_{PPh,ortho}$), 130.8 (d, $^1J_{CP}$ = 217.4 Hz; $C_{PPh,ipso}$), 131.3 (d, $^2J_{CP}$ = 12.0 Hz; $CH_{PPh,ortho}$), 131.9 (d, $^4J_{CP}$ = 3.13 Hz; $CH_{PPh,para}$), 132.1 (d, $^4J_{CP}$ = 3.09 Hz; $CH_{PPh,para}$), 134.2 (d, $^2J_{CP}$ = 9.48 Hz; $CH_{Ru-PPh,ortho}$), 135.3 (d, $^2J_{CP}$ = 10.62 Hz; $CH_{Ru-PPh,ortho}$), 136.2 (dd, $^1J_{CP}$ = 34.7, $^4J_{CP}$ = 0.96 Hz; $C_{PPh,ipso}$), 137.0 (dd, $^1J_{CP}$ = 43.9, $^4J_{CP}$ = 1.17 Hz; $C_{PPh,ipso}$), 144.2 ($CH_{SPPh-C5}$), 150.9 ($C_{SPPh,ipso}$). The signal of the central carbon atom (PCS) could not be detected in the ^{13}C NMR spectrum, but in the HSQC via correlation with the multiplet at δ = 2.86−2.90 ppm in the ^{1}H NMR spectrum, corresponding to the proton at the metalated carbon atom. ^{31}P{^{1}H} NMR (162.0 MHz, CD_2Cl_2): δ 45.6 (dd, $^4J_{PP}$ = 25.7 Hz, $^3J_{PP}$ = 7.39 Hz; $SPPh_2$), 55.3 (d, $^3J_{PP}$ = 7.38 Hz; PPh_3), 68.1 (d, $^3J_{PP}$ = 25.6 Hz; PPh_3). Anal. Calcd for $C_{55}H_{45}O_2P_3RuS_2$: C, 66.32; H, 4.55; S, 6.44. Found: C, 66.30; H, 4.80; S, 6.16.

X-ray Crystallographic Studies. Data collection of all compounds was conducted with a Bruker APEX-CCD (D8 three-circle goniometer). The structures were solved using direct methods, refined with the SHELX software package,[23] and expanded using Fourier techniques. The crystals of the two compounds were mounted in an inert oil (perfluoropolyalkyl ether). Crystal structure determinations were effected at 100 K. The structure was solved applying direct and Fourier methods, using SHELXS-90 (G. M. Sheldrick, University of Göttingen 1990) and SHELXL-97 (G. M. Sheldrick, SHELXL97, University of Göttingen 1997). Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-980200 (**2**) and CCDC-980201 (**4**). Data collection and structure refinement details are provided in the SI.

Computational Studies. All calculations were performed without symmetry restrictions except for the planar isomer **2′**. Starting coordinates were obtained with Chem3DUltra 10.0 or directly from the crystal structure analysis. All calculations were done with the Gaussian 03 (Revision E.01) program package.[24] Geometry optimizations were performed using density functional theory (DFT) with the B3LYP (Becke 3-parameter−Lee−Yang−Parr) functional[25] and the LANL2Tz(f) basis set for Zr, Pd, and Ru and the 6-311+G(d,p) basis set for all other atoms. Comparative studies were performed with the BP86 functional and the TZVP basis set (see the SI). Harmonic vibrational frequency analyses were performed at the same levels of theory. The vibrational frequency analyses showed no imaginary frequencies for the ground states and a single negative frequency for the transition states. Transition states were located by using the qst3 method or the opt=modred keyword and subsequent optimization of the imaginary frequency. NBO analyses were carried out on the optimized structures at the same level of theory using the NBO 5.0 program interfaced to the Gaussian 03 package.[21] For further details, see the SI.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Complete experimental procedures, analytical data, and NMR spectra for all new compounds; crystallographic and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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