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Lewis Acid Base Chemistry of Bestmann's Ylide, Ph_3PCCO, and its Bulkier Analogue, $(Cyclohexyl)_3PCCO$

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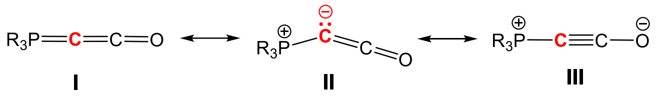
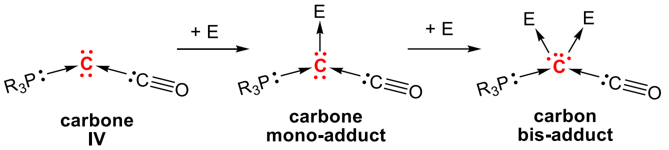
The new phosphoranylideneketene, $(cyclohexyl)_3PCCO$, was synthesized and structurally as well as spectroscopically characterized. Ph_3PCCO and $(cyclohexyl)_3PCCO$ were found to be weak ambidentate Lewis bases capable of donating to strong Lewis acids via the ylidic carbon or the carbonyl oxygen.

Triphenylphosphoranylideneketene, Ph_3PCCO, also referred to as Bestmann's ylide is a molecule of remarkable chemical versatility. It has found widespread use as a chemical linchpin reagent for the synthesis of various natural products [1] and was found to undergo [2+2] and [2+4] cycloaddition reactions [2]. Ph_3PCCO is best described by three resonance structures (Scheme 1), of which ylide **II** plays an important role as X-ray crystallographic studies have revealed the bent structure of Ph_3PCCO [3].



Scheme 1. Valid resonance structures of $R_3P=C=C=O$ [6].

Recently, Frenking et al. proposed the bonding in Ph_3PCCO to be viewed as donor-acceptor interactions between the closed shell ligands PPh_3, CO and a carbon atom with two lone pairs ($Ph_3P \rightarrow C \leftarrow CO$), (**IV**) and classified Ph_3PCCO as a "carbone", a divalent carbon compound with carbon in formal oxidation state 0 (Scheme 2) [4]. Based on computational data, the same group suggested that both lone pairs at the divalent carbon(0) might be available for double protonation or donation to two electrophilic main group or transition metal fragments (Scheme 2) [4]. However, the few experimental data [5, 6] appear to suggest otherwise as so far only one transition metal fragment could be attached to the ylidic carbon of Ph_3PCCO [7]. Moreover, attempts to protonate Ph_3PCCO gave rise to [2+2] cycloaddition products [2c], rendering the doubly protonated dication $[Ph_3P \rightarrow CH_2 \leftarrow CO]^{2+}$ an elusive species.



Scheme 2. Dative bond description of R_3PCCO (**IV**) and carbone adduct formation proposed by Frenking et al. ($E = H^+$, BH_3, $Ni(CO)_3$) [4].

Curiously, stable Lewis acid-base adducts of Ph_3PCCO with main group element compounds have not been reported either [8]. This prompted us to investigated the donor behaviour of Ph_3PCCO (**1**) and its bulkier analogue, $(cyclohexyl)_3PCCO$ (**2**), in the presence of various organoboranes and alanes. The new ylide $(cyclohexyl)_3PCCO$ (**2**) was synthesized via the reaction of $[(cyclohexyl)_3PCH_2COOEt]Br$ with two equiv. of $NaN(SiMe_3)_2$ in toluene as solvent and isolated in yields of 70% (ESI). The solid-state structure of **1** was re-determined (Fig. 1, left) as non-satisfactory R_1-values (R_r = 9.2%) were obtained from previously reported data collections [3]. In fact, data re-collection and refinement resulted in an improved R_1 value (3.4%) and longer P=C, C=C and C=O bond lengths of 1.671(2), 1.247(2) and 1.195(2) Å, resp., (Table 1) compared to previous data with 1.648(7) (P=C), 1.210(10) (C=C) and 1.185(9) Å (C=O) [3].

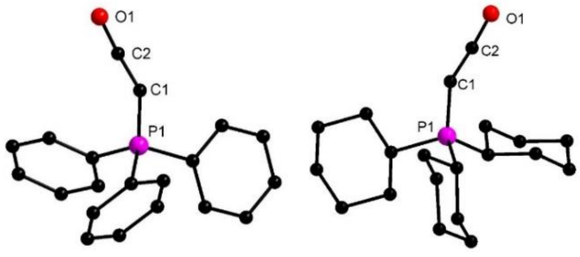


Figure 1. Solid-state structures of **1** (left) and **2** (right) [H atoms omitted for clarity].

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Electronic Supplementary Information (ESI) available: [Crystal data and structure refinement of **1**-**3**, **5**-**7**, **10** and **11** (CCDC 1881945-1881952), synthetic procedures and characterization data of **2**-**11**]. See DOI: 10.1039/x0xx00000x

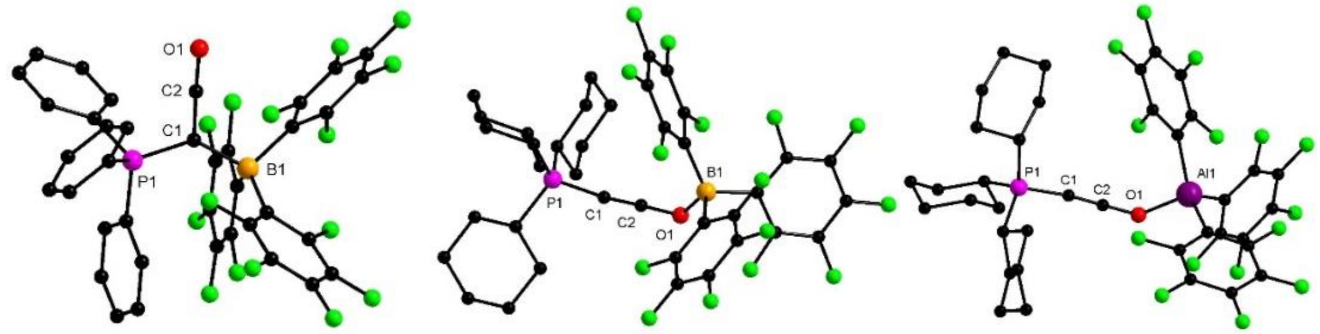
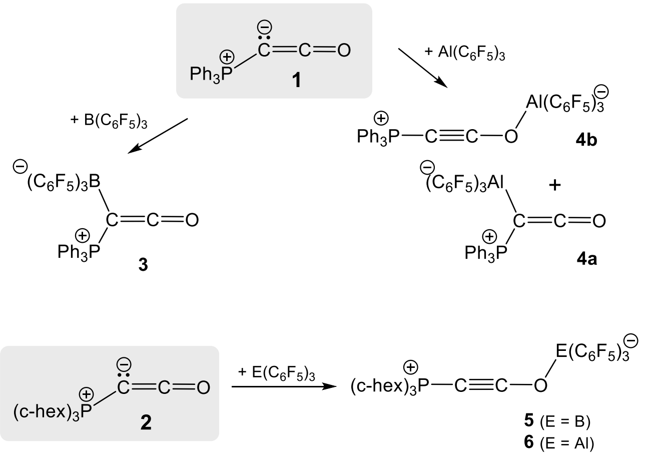


Figure 2. Solid-state structures of **3** (left), **5** (middle) and **6** (right) [H atoms omitted for clarity; black = carbon; green = fluorine].

Despite the increased bulkiness of the phosphonium group in **2**, the structural parameters of **1** and **2** were strikingly similar to each other (Table 1) [8]. This is consistent with the similar Raman and IR spectra of **1** and **2** showing absorptions at 2085 cm^{-1} and 2086 cm^{-1}, resp., for the asymmetric CCO stretch and less intense signals at 1437 and 1444 cm^{-1}, resp., for the symmetric CCO stretch (Table 2 and ESI). In the ^{13}C NMR the ylidic carbon of **2** appears at –18.4 pm with a scalar C-P coupling constant of 177 Hz, again, similar to what is seen for **1** with the respective signal at -9.7 ppm ($^{1}J_{\text{C-P}}$ = 194 Hz) in C_6D_6 as solvent.

After having established the structural parameters and spectroscopic properties of **1** and **2** their ability to form stable Lewis acid-base adducts with the strong Lewis acids $B(C_6F_5)_3$ and $Al(C_6F_5)_3$, resp., was evaluated (Scheme 3). Thus, upon adding $B(C_6F_5)_3$ to a benzene solution of **1** a crystalline material precipitated from solution, which by multi-nuclear NMR spectroscopy and the results of an X-ray analysis was identified as adduct **3** (Fig. 2 left).



Scheme 3. Formation of the Lewis acid base adducts **3**-**6**.

The solution ^{11}B, ^{19}F and ^{31}P NMR data confirmed the formation of **3** as an inner salt with a tetra-coordinated borate anion and a phosphonium cation. It was not possible to detect the signal of the ylidic carbon in the ^{13}C NMR spectrum most likely due to additional coupling with the adjacent quadrupolar ^{11}B nucleus. Nonetheless, the X-ray data clearly confirmed bonding between the ylidic carbon and boron [C1-B1, 1.705(1) Å], resulting in increased P1-C1 and C1-C2 distances relative to those in **1**. The C=O bond significantly shortened upon adduct formation from 1.195(2) Å in **1** to 1.163(3) Å in **3**, in line with an increased wavenumber of the asymmetric CCO stretch from 2085 cm^{-1} for **1** to 2096 cm^{-1} for **3**.

Table 1. Selected bond lengths [Å] and angles [°] of **1**-**3**, **5** and **6**.

-	**1**	**2**	**3**	**5**	**6**
P1-C1	1.671(2)	1.676(1)	1.752(3)	1.701(3)	1.698(2)
C1-C2	1.247(2)	1.248(2)	1.316(4)	1.192(4)	1.207(2)
C2-O1	1.195(2)	1.200(2)	1.163(3)	1.265(3)	1.258(2)
P1-C1-C2	143.1(1)	140.1(1)	110.5(2)	172.8(3)	173.9(2)
C1-C2-O1	174.8(2)	174.6(1)	177.0(3)	176.7(3)	179.7(2)

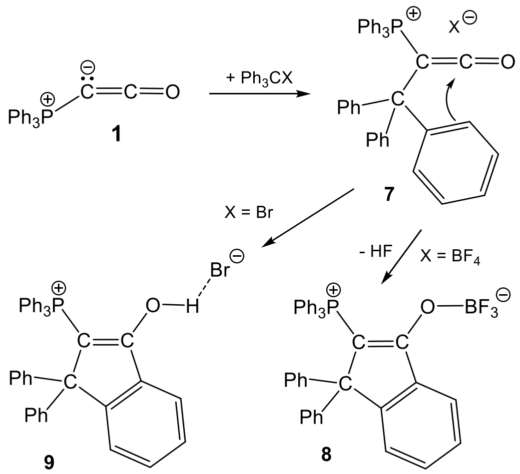
Table 2. Selected ^{31}P and ^{13}C NMR chemical shifts [δ in ppm], C-P coupling constants [J in Hz] and CCO stretching frequencies [ν in cm^{-1}] of **1-3**, **5** and **6**.

-	**1**	**2**	**3**	**5**	**6**
$\delta(^{31}P)_{\mathbf{P}=C=C=O}$	2.6	20.5	29.9	23.9	24.5
$\delta(^{13}C)_{P=\mathbf{C}=C=O}$	-9.7	-17.5	-	5.2	0.0
$^{1}J_{C,P}$	194	177	-	200	202
$\delta(^{13}C)_{P=C=\mathbf{C}=O}$	147.7	145.5	171.9	125.3	124.5
$^{2}J_{C,P}$	44	39	10	40	41
ν_{CCO} (asym.)	2085	2086	2096	2187	2205

Treatment of the sterically more hindered ylide **2** with $B(C_6F_5)_3$ and $Al(C_6F_5)_3$, resp., furnished the Lewis acid-base adducts **5** (80%) and **6** (65%) as the sole products as confirmed by multi-nuclear NMR spectroscopy and X-ray analysis (Figure 2). In the ^{13}C NMR the ylidic carbon of the boron adduct **5** appears at 4.2 pm with a scalar C-P coupling constant of ca. 200 Hz, similar to what is seen for the aluminium adduct **6** with the respective signal at -1.3 ppm ($^{1}J_{\text{C-P}}$ = 202 Hz) in C_6D_6 as solvent. Note also that the chemical shifts of the phosphonium signals in the ^{31}P NMR of **5** (23.9 ppm) and **6** (24.5 ppm) are similar to ylide **2** (20.5 ppm), suggesting only small changes in the electronic environment of phosphorous upon coordination of the Lewis acid fragment. This notion is further supported by the X-ray data showing only a slight increase of the P-C distances from 1.676(1) Å in ylide **2** to 1.701(3) and 1.698(2) Å in the adducts **5** and **6**, resp. The data also confirm that the carbonyl oxygen's bind to the Lewis acid fragments with a B-O distance of 1.573(3) Å for **5** and an Al-O distance of 1.820(1) Å for **6**, strikingly different from what is seen for **3**, where $B(C_6F_5)_3$ binds to the ylidic carbon. The reason appears to be steric in nature as the bulkier cyclohexyl groups at phosphorous provide a much better steric protection rendering adduct formation at the ylidic carbon less favourable. Other notable structural features are the almost linear P1-C1-C2-O1 units with elongated C2-O1 bonds and very short C1-C2 distances of 1.192(4) Å for **5** and 1.207(2) Å for **6** indicative of the triple bond character of the C1-C2 bond. That the C1-C2 bonds in **5** and **6** are shorter than in **1** and **2** is in good agreement with the IR spectra, showing the asymmetric CCO stretches of **5** (2187 cm^{-1}) and **6** (2205 cm^{-1}) to be at significantly higher frequencies than those of the ylides **1** (2085 cm^{-1}) and **2** (2086 cm^{-1}) (Table 2). Note that the frequency values for **5** and **6** are very similar to those of organic alkynes with C≡C stretches being in the range of 2150-2250 cm^{-1}. In contrast, **3** features an ylidic carbon with a distorted trigonal planar geometry, an elongated C1-C2 bond [1.316(4) Å] and a shortened C2-O1 distance (1.16 Å) indicating increased double bond character of the C=O bond. This is consistent with the observed CCO stretching frequency of **3** at 2096 cm^{-1}, being slightly higher in energy than those of the ylides **1** and **2**, and similar to what is seen for asymmetric stretches of organic ketenes, $R_2C=C=O$ [9].

It was not possible to isolate a stable product from the reaction of **1** with $Al(C_6F_5)_3$ as these solutions slowly decomposed. Nonetheless, the ^{19}F NMR data of a freshly prepared solution of **1** and $Al(C_6F_5)_3$ suggested a tetra-coordinated $Al(C_6F_5)_3$ consistent with the formation of a Lewis acid-base adduct. The ^{31}P NMR spectrum showed an extremely broad signal at ca. 10 ppm, which upon cooling to -60°C splits into two sharper still relatively broad signals at 28 and 4 ppm, indicating rapid exchange of $Al(C_6F_5)_3$ between the ylidic carbon and the carbonyl oxygen. This notion is supported by the solid-state IR data, which showed two absorptions at 2096 cm^{-1} and 2189 cm^{-1}, suggesting the formation of the ylidic carbon adduct $(Ph_3P)[(C_6F_5)_3Al]C=C=O$ (**4a**) and the corresponding carbonyl adduct $Ph_3P\text{-}C\equiv C\text{-}OAl(C_6F_5)_3$ (**4b**).

We were interested in whether **1** would react with carbo-cationic Lewis acids to form stable phosphonium ketenes, so far elusive species. Previous investigations [2] revealed that upon alkylation of the ylidic carbon of **1** with primary alkyl halides, phosphonium ketenes intermediately formed, which rapidly reacted with additional **1** to give products of formal 2+2 cycloaddition. To prevent the phosphonium ketene from undergoing 2+2 cycloaddition, **1** was reacted with the bulkier electrophiles Ph_3CBr and Ph_3CBF_4, resp., in CH_3CN as solvent [10]. Monitoring the reactions by ^{31}P NMR spectroscopy showed indeed the initial formation of the ketenes **7**, which proved to be unstable as the respective phosphorous signals in the ^{31}P-NMR spectrum at 25.2 ppm disappeared within a couple of hours (Scheme 4). Simultaneously, crystalline precipitates formed, which were isolated and identified by multi-nuclear NMR spectroscopy and X-ray analyses (Fig. 4) as the phosphonium enolates **8** (62%) and **9** (53%). The C1-C2 distances of **8** and **9** were found to be 1.375(4) and 1.361(2) Å consistent with the formulation of the C1-C2 bond as a double bond for both compounds. The assignment as enolate structures is further supported by the elongated C1-P1 and C2-O1 distances for both molecules and the IR data, showing an OH stretch for **9** (ν = 3300 cm^{-1}) and the absence of any C=O stretches for **8** and **9**. The generation of **8** and **9** can be rationalized by an intramolecular Friedel-Crafts reaction of the formed ketene intermediates **7** via nucleophilic attack of one of the Ph_3C phenyl groups at the carbonyl carbons of the ketene units.



Scheme 4. Formation of **8** and **9**.

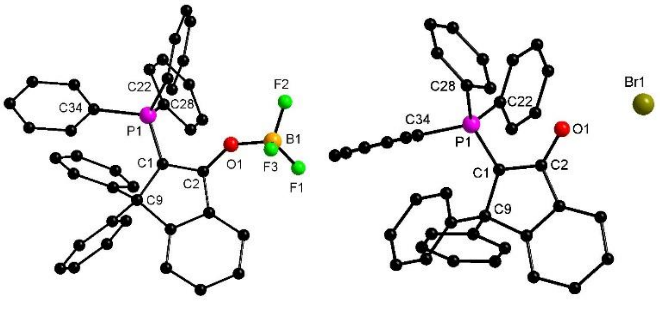
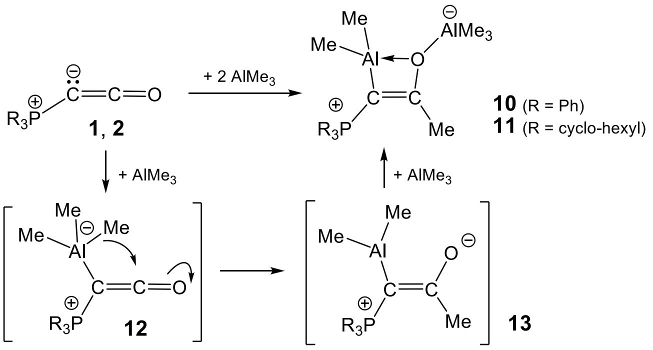


Figure 3. Solid-state structures of **8** (left) and **9** (right) [H atoms omitted for clarity]. Selected distances [Å] and angles [°]: **8**: P1-C1 1.760(3), O1-C2 1.319(3), O1-B1 1.495(4), C1-C2 1.375(4), C1-C9 1.539(4), C2-O1-B1 126.8(2), O1-C2-C3 128.1(3), C2-C1-P1 118.0(2); **9**: P1-C1 1.7684(16), C1-C2 1.361(2), C2-O1 1.328(2), C1-C9 1.541(2), C2-C1-P1 117.85(12), O1-C2-C1 122.90(15).

Note that in none of the above reactions have we observed the formation of adducts that contain two Lewis acid fragments, neither at the carbonyl oxygen nor at the ylidic carbon as calculated for the hypothetical carbone bis-adduct $(Ph_3P)(OC)C(BH_3)_2$ (Scheme 2) [4]. Certainly, despite being exceptionally strong Lewis acids, $B(C_6F_5)_3$ and $Al(C_6F_5)_3$ are far too bulky to permit the formation of such binuclear Lewis acid base adducts. However, attempts to generate carbone bis-adducts from reactions of **1** with boron based Lewis acids of smaller size such as BPh_3, BEt_3 or $B(OMe)_3$ failed as well, most likely due to their significantly lower Lewis acidity. Even over prolonged periods of time and at elevated temperatures, no reaction occurred as judged by ^{31}P and ^{11}B NMR spectroscopy. Also reactions of BH_3 with **1** and **2**, resp., under various conditions did not give the expected adducts $(Ph_3P)(BH_3)C=C=O$ or $Ph_3P\text{-}C\equiv C\text{-}O\text{-}BH_3$ nor Frenking's predicted carbone bis-adduct $(Ph_3P)(OC)C(BH_3)_2$ [4], instead, decomposition and formation of unidentified hydroboration products was noted. Upon adding two equivalents of $AlMe_3$ to benzene solutions **1** and **2**, resp., crystals precipitated from solution, which by multi-nuclear NMR spectroscopy and the results of an X-ray analysis were identified as the binuclear compounds **10** and **11** (Scheme 5). The X-ray data of **10** (Fig. 3) and **11** [ESI] confirm connectivity and reveal for **10** an intramolecular coordination of the carbonyl oxygen to the $AlMe_2$ moiety. Again, the short C1-C2 distance of 1.342(2) Å and the elongated P1-C1 bond is in agreement with the formulation of a C=C double bond. Both compounds proved thermally unstable and slowly decomposed in solution as well as in the solid state. Their formation can be understood in terms of initial formation of Lewis acid-base adduct **12**, which upon migration of a methyl group from aluminium to the carbonyl carbon generates the enolate **13**. Coordination of a second molecule of $AlMe_3$ to the enolate oxygen of **13** finally leads to the formation of **10** and **11**.



Scheme 5. Formation of **10** and **11**.

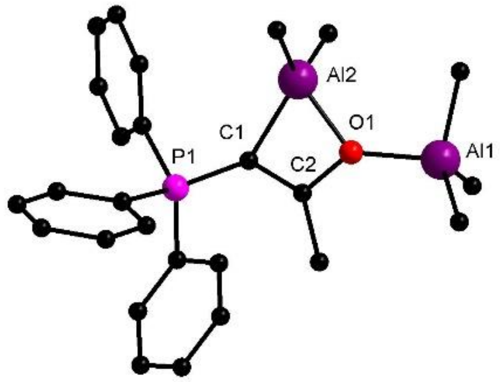
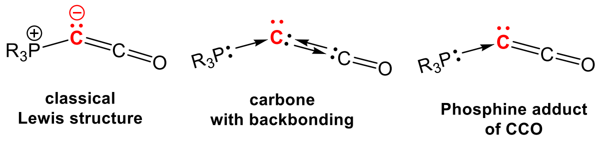


Figure 4. Solid-state structure of **10** (H atoms omitted for clarity). Selected distances [Å] and angles [°]: P1-C1 1.7211(17) Al1-O1 1.8867(13), Al2-O1 1.9179(13), Al2-C1 2.0083(18), O1-C2 1.3837(19), C1-C2 1.342(2), Al1-O1-Al2 131.24(6), C2-C1-P1 129.60(14), P1-C1-Al2 141.85(10), C2-C1-Al2 88.29(11), O1-Al2-C1 69.73(6), C2-O1-Al1 135.03(10), C1-C2-O1 110.91(15).

In conclusion, R_3PCCO can be viewed as relatively weak ambidentate Lewis donors forming labile Lewis acid-base adducts with strong Lewis acids via the ylidic carbon or the carbonyl oxygen. The inability of these ylides to form stable adducts with weakly Lewis acidic boranes and stable carbone bis-adducts suggests that a dative bond description of R_3PCCO as $Ph_3P\rightarrow C\leftarrow CO$ (**IV**) with two lone pairs localized at the central carbon is of limited use. Given that the CCO stretching frequencies of R_3PCCO are significantly lower than that of CO, a description of R_3PCCO as a carbone with back bonding to CO as shown in Scheme 6 appears to be more appropriate. Alternatively, R_3PCCO can be viewed as $R_3P\rightarrow C=C=O$, a Lewis acid-base adduct of R_3P and dicarbon monoxide (:C=C=O), the latter found in interstellar space [11], [12]



Scheme 6. R_3PCCO - Classical Lewis structure versus dative bond descriptions for R_3PCCO.

Conflicts of interest

There are no conflicts to declare.

Notes and references

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1 a) G. Han, M. G. LaPorte, J. J. Folmer, K. M. Werner and S. M. Weinreb, *J. Org. Chem.*, **2000**, 65, 6293; b) G. Stork, F. West, H. Y. Lee, R. C. A. Isaacs and S. Manabe, *J. Am. Chem. Soc.*, **1996**, *118*, 10660; c) H. Zhang, M. S. Reddy, S. Phoenix and P. Deslongchamps, *Angew. Chem., Int. Ed.*, **2008**, *47*, 1272; d) A. Raghuraman, E. Ko, L. M. Perez, T. R. Ioerger and K. Burgess, *J. Am. Chem. Soc.*, **2011**, *133*, 12350; e) Y. Yang, Y. Bai, S. Sun and M. Dai, *Org. Lett.*, **2014**, *16*, 6216: f) R. M. Risi and S. D. Burke, *Org. Lett.*, **2012**, *14*, 1180.

2 a) G. H. Birum and C. N. Matthews, *J. Am. Chem. Soc.* **1968**, *90*, 3842; b) H. J. Bestmann, C. Geismann and R. Zimmermann, *Chem. Ber.*, **1994**, *127*, 1501; c) H. J. Bestmann, G. Schmid, D. Sandmeier and L. Kisielowski, *Angew. Chem.* **1977**, 89, 275.

3 J. J. Daly and P. J. Wheatley, *J. Chem. Soc. A: Inorg., Phys., Theor.* **1966**, 1703.

4 a) R. Tonner and G. Frenking, *Chem. Eur. J.* **2008**, *14*, 3260; b) R. Tonner and G. Frenking, *Chem. Eur. J.* **2008**, *14*, 3273; c) G. Frenking and R. Tonner, *Pure Appl. Chem.* **2009**, *81*, 597; d) R. Tonner and G. Frenking, *Organometallics* **2009**, *28*, 3901; L. Zhao, M. Hermann, N. Holzmann and G. Frenking, *Coord. Chem. Rev.*, **2017**, 344, 163.

5 M. Alcarazo, C. W. Lehmann, A. Anoop, W. Thiel and A. Fuerstner, *Nature Chemistry*, **2009**, *1*, 295.

6 a) R. Bertani, M. Casarin and L. Pandolfo, *Coord. Chem. Rev.*, **2003**, *236*, 15; b) L. Pandolfo, G. Paiaro, L. K. Dragani, C. Maccato, R. Bertani, G. Facchin, L. Zanotto, P. Ganis and G. Valle, *Organometallics*, **1996**, *15*, 3250.

7 For the addition of a Sn(II) compound across the C=C bond of Ph_3PCCO see: H. Gruetzmacher, W. Deck, H. Pritzkow and M. Sander, *Angew. Chem., Int. Ed. Engl.*, **1994**, *33*, 456.

8 F. Lavigne, E. Maerten, G. Alcaraz, V. Branchadell, N. Saffon-Merceron and A. Baceiredo, *Angew. Chem., Int. Ed.*, **2012**, *51*, 2489.

9 a) M. McAllister and T. T. Tidwell, *Can. J. Chem.*, **1993**, *72*, 882; b) S. V. Chekalin, V. O. Kompanets, V. B. Laptev, S. V. Pigulsky, A. A. Makarov and E. A. Ryabov, *Chem. Phys. Lett.* **2011**, *512*, 178.

10 P. A. Byrne, K. Karaghiosoff and H. Mayr, *J. Am. Chem. Soc.*, **2016**, *138*, 11272.

11 a) M. Ohishi, H, Suzuki, S. I. Ishikawa, C. Yamada, H. Kanamori, W. M. Irvine, R. D. Brown, P. D. Godfrey and N. Kaifu, *Astrophys. J.*, **1991**, *380*, L39; b) R. D. Brown, D. M. Cragg, P. D. Godfrey, W. M. Irvine, D. McGonagle and M. Ohishi, *Evol. Biospheres*, **1992**, *21*, 399.

12 K. Bayes, *J. Am. Chem. Soc.* **1961**, 83, 3712.