

## Organophosphorus Chemistry

## A Direct, Modular, and Efficient Construction of the P—C—P Structural Motif through Coupling of Manganese Carbyne Complexes with Phosphines

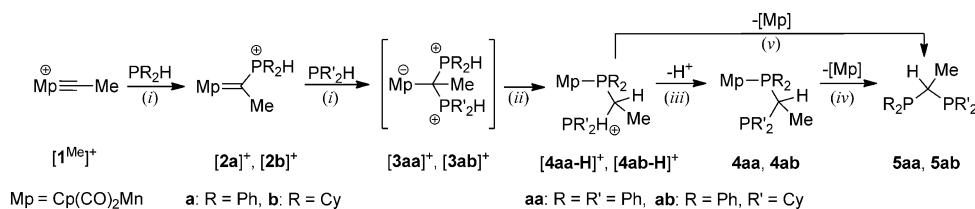
Dmitry A. Valyaev,<sup>[a, b]</sup> Stéphanie Bastin,<sup>[a, b]</sup> Kamil I. Utegenov,<sup>[c]</sup> Noël Lugan,\*<sup>[a, b]</sup>  
Guy Lavigne,<sup>[a, b]</sup> and Nikolai A. Ustyryuk<sup>[c]</sup>

**Abstract:** Easily available carbyne complexes of manganese were used as a source of carbyne fragments in an unconventional synthesis of backbone-substituted diphosphinomethanes and cyclic P-ylides upon coupling with secondary or tertiary phosphines, respectively, followed by demetalation under mild conditions.

To date, transition-metal phosphoniocarbene complexes  $L_nM=C(R)PR'_3^+$ , which are easily available from electrophilic carbyne precursors and phosphines,<sup>[1, 2]</sup> have found only limited application in synthetic chemistry, with the notable exception of Grubbs type ruthenium phosphoniocarbene complexes being among the most active initiators in olefin metathesis.<sup>[2, 3]</sup> Yet, a further exploitable aspect of their reactivity rests on the strong electrophilicity of their carbonic atom—inherent to the presence of the adjacent positively charged phosphorus fragment—favoring further coupling with incoming nucleophiles.<sup>[4]</sup> Based on this, we report herein a conceptually new route to backbone-substituted diphosphinomethane and cyclic P-ylide derivatives using a fully controlled stepwise carbyne/phosphine/phosphine coupling involving  $Mn^1$  phosphoniocarbene complexes as key reactive species.

We first observed that the  $Mn^1$  phosphoniocarbene complex  $[Mp=C(Me)PPH_2H]BCl_4$  (**2a**) $BCl_4$  (here and thereafter,  $Mp = Cp(CO)_2Mn$ ) generated in situ upon addition of  $PPH_2H$  to the methylcarbyne precursor  $[Mp\equiv CMe]BCl_4$ , [**1<sup>Me</sup>**] $BCl_4$  at low temperature,<sup>[1b,d,e]</sup> can uptake a second molecule of phosphine to give the cationic complex **4aa-H** $BCl_4$  featuring a newly formed pendant P—C—P structural motif containing ligand resulting formally from the coupling of the carbyne fragment and two secondary phosphines (Scheme 1). Deprotonation of the latter upon purification on an alumina column afforded a neutral diphosphine complex **4aa** in a nearly quantitative yield.

The **2a** $BCl_4 \rightarrow 4aa transformation is likely to proceed via the formation of an elusive semi-ylide intermediate, **[3aa]** $BCl_4$ ,<sup>[5]</sup> resulting from the nucleophilic attack of the$



**Scheme 1.** Coupling of  $[Mp\equiv CMe]BCl_4$  with two equivalents of secondary phosphines ( $BCl_4^-$  anions omitted for clarity). Conditions: i)  $CH_2Cl_2, -80^\circ C$ . ii) Warming to RT. iii) Deprotonation with  $Al_2O_3$  (**4aa**) or  $Et_3N$  (**4ab**). iv)  $HBF_4 \cdot OEt_2$  (2 equiv),  $h\nu$ ,  $CH_2Cl_2$ . v)  $h\nu$ ,  $CH_2Cl_2$ .

second  $PPH_2H$  molecule onto the highly electrophilic carbene atom, the latter undergoing a proton migration from the phosphonium fragment to the central carbon atom with concomitant metal coordination to form the protonated diphosphine complex **[4aa-H]** $BCl_4$ , ultimately giving **4aa** upon deprotonation. Though the key irreversible transformation **[3aa]** $BCl_4 \rightarrow [4aa-H]$  $BCl_4$  may proceed through the stepwise formation of a manganese *cis*-hydride species by 1,3-H shift followed by reductive elimination,<sup>[6]</sup> the occurrence of a direct concerted 1,2-proton migration from the phosphonium moiety to the ylidic carbon remains an alternate mechanistic possibility.

Stepwise addition of molar equivalents of  $PPH_2H$  followed by  $PCy_2H$  to **[1<sup>Me</sup>** $BCl_4$  at  $-80^\circ C$  led in the end to a mixture of two diphosphine complexes **4aa** and **4ab** in approximately 1:2.5 ratio (Scheme 1), finally isolated in 18% and 49% yield, respectively (see the Supporting information for details of the **4aa**/

[a] Dr. D. A. Valyaev, S. Bastin, N. Lugan, G. Lavigne  
Laboratoire de Chimie de Coordination du CNRS (UPR 8241)  
205 route de Narbonne, BP 44099, 31077 Toulouse Cedex 4 (France)  
Fax: (+33) 561553003  
E-mail: noel.lugan@lcc-toulouse.fr

[b] Dr. D. A. Valyaev, S. Bastin, N. Lugan, G. Lavigne  
Université de Toulouse, UPS, INPT, 31077 Toulouse Cedex 4 (France)

[c] K. I. Utegenov, Prof. Dr. N. A. Ustyryuk  
A. N. Nesmeyanov Institute of Organoelement Compounds (INEOS)  
Russian Academy of Sciences  
28 Vavilov str., GSP-1, B-334, Moscow (Russia)

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/chem.201304239>.

**4ab** separation). Gratifyingly, the inversion of the order of phosphines addition—that is,  $\text{PCy}_2\text{H}$  followed by  $\text{PPh}_2\text{H}$ —allowed to optimize the heterocoupling process affording **4ab** in 93% isolated yield (**4aa/4ab** ratio in the crude product was ca. 1:50). Interestingly, regardless of the order of phosphines addition, the diphosphine ligand in **4ab** was systematically found coordinated to the metal through the  $\text{PPh}_2$  moiety, which is consistent with the occurrence of a proton migration in  $[\mathbf{3ab}]\text{BCl}_4$  from the less basic phosphonium site. The structure of **4ab** featuring the pendant  $\text{PCy}_2$  termination was confirmed by single-crystal XRD (Figure 1).<sup>[7]</sup>

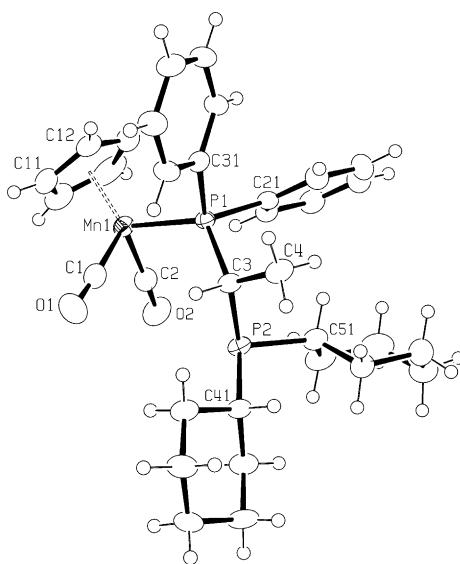


Figure 1. A perspective view of **4ab** (ellipsoids at the 30% probability level).

The selectivity observed in  $\text{PPh}_2\text{H}/\text{PCy}_2\text{H}$  coupling can be reasonably ascribed to the different electrophilic and steric properties of the phosphoniocarbene intermediates. Unlike  $[\mathbf{2a}]\text{BCl}_4$  showing the uptake of both phosphines at very low temperature ( $-80^\circ\text{C}$ ), the reaction of the less electrophilic and more bulky  $[\mathbf{2b}]\text{BCl}_4$  with  $\text{PPh}_2\text{H}$  takes place only between  $-20\text{--}0^\circ\text{C}$ , leading to the rapid  $[\mathbf{3ab}]\text{BCl}_4 \rightarrow [\mathbf{4ab-H}]\text{BCl}_4$  rearrangement. The lower selectivity observed in the reaction of  $[\mathbf{2a}]\text{BCl}_4$  with  $\text{PCy}_2\text{H}$  at  $-80^\circ\text{C}$  could be explained by a partial scrambling of the semi-ylide complex  $[\mathbf{3ab}]\text{BCl}_4$  under such reaction conditions ( $[\mathbf{2a}]\text{BCl}_4 + \text{PCy}_2\text{H} \rightleftharpoons [\mathbf{3ab}]\text{BCl}_4 \rightleftharpoons [\mathbf{2b}]\text{BCl}_4 + \text{PPh}_2\text{H}$ ) to form some  $\text{PPh}_2\text{H}$  rapidly trapped by complex  $[\mathbf{2a}]\text{BCl}_4$ .

Having in mind the aim to exploit this original carbyne/phosphine/phosphine coupling for the synthesis of valuable chemicals, we next focused on means to efficiently liberate the resulting diphosphines from the robust manganese complexes (**4** → **5**, Scheme 1). Inspired by the high yield photochemical liberation of cyclopentadienes<sup>[8]</sup> or allene<sup>[6b]</sup> from cymantrene derivatives, we first investigated the behavior of the model complex  $\text{Mp}(\text{PPh}_3)$  (**6**) under visible light irradiation in different solvents (Table 1).

Complex **6** appeared to be stable upon prolonged irradiation in toluene. Conversely, its irradiation in THF after approxi-

Table 1. Photochemical demetalation of  $\text{Mn}^{\text{l}}$  complexes **6**, **4aa**, and  $[\mathbf{4ab-H}]\text{BF}_4$ .<sup>[a]</sup>

Complex	Solvent	Additive	Time	Product	Yield [%]
<b>6</b>	toluene	—	4 h	$\text{PPh}_3$	traces
<b>6</b>	THF	—	30 min	$\text{PPh}_3$ $\text{Mp}(\text{THF})$	60 <sup>[b]</sup> 60 <sup>[b]</sup>
<b>6</b>	THF	$\text{BH}_3\cdot\text{SMe}_2$ <sup>[d]</sup>	1 h	$\text{PPh}_3\cdot\text{BH}_3$ $\text{Mp}(\text{SMe}_2)$	95 <sup>[c]</sup> 76 <sup>[c]</sup>
<b>6</b>	$\text{CH}_2\text{Cl}_2$	—	10 min	$\text{PPh}_3$	92 <sup>[c]</sup>
<b>6</b>	toluene	$\text{CH}_2\text{Cl}_2$ <sup>[e]</sup>	45 min	$\text{PPh}_3$	85 <sup>[c]</sup>
<b>4aa</b>	$\text{CH}_2\text{Cl}_2$	—	4 h	<b>5aa</b>	19 <sup>[c]</sup>
<b>4aa</b>	$\text{CH}_2\text{Cl}_2$	$\text{BH}_3\cdot\text{SMe}_2$ <sup>[f]</sup>	40 min	<b>5aa</b> <sup>[h]</sup>	88 <sup>[c]</sup>
<b>4aa</b>	$\text{CH}_2\text{Cl}_2$	$\text{HBF}_4\cdot\text{OEt}_2$ <sup>[g]</sup>	15 min	<b>5aa</b> <sup>[i]</sup>	90 <sup>[c]</sup>
$[\mathbf{4ab-H}]\text{BF}_4$	$\text{CH}_2\text{Cl}_2$	—	10 min	<b>5ab</b> <sup>[i]</sup>	97 <sup>[c]</sup>

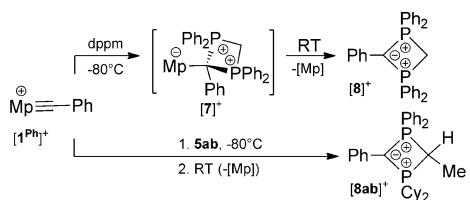
[a] Photolysis of 8–12 mM solution of  $\text{Mn}^{\text{l}}$  phosphine complex in 125 mL of the appropriate solvent with immersed medium pressure Hg lamp (150 W) using Pyrex filter jacket at 15–20 °C for the indicated time period. [b] Yield estimated by IR spectroscopy in the  $\nu(\text{CO})$  region. [c] Yield of the isolated product. [d] 1.25 equiv. [e] 1% vol. [f] 2.5 equiv. [g] 2.0 equiv. [h] After deboronation with DABCO. [i] After deprotonation with 2 M  $\text{NaOH}_{\text{aq}}$ .

mately 30 min led to an equilibrium mixture of **6**,  $\text{PPh}_3$  and  $\text{Mp}(\text{THF})$ . This equilibrium could be easily shifted to the right upon addition of  $\text{BH}_3\cdot\text{SMe}_2$  as a phosphine scavenger, to afford  $\text{PPh}_3\cdot\text{BH}_3$  and  $\text{Mp}(\text{SMe}_2)$  in good yield. This represents the first evidence for a selective  $\text{PPh}_3$  ligand photodissociation upon bulk photolysis of  $\text{Mp}(\text{PR}_3)$  complexes.<sup>[9]</sup> We were pleased to observe that the irradiation of **6** in  $\text{CH}_2\text{Cl}_2$  caused its very rapid destruction with liberation of  $\text{PPh}_3$  and formation of an insoluble metal-containing product. As a working hypothesis, we considered that this decomplexation process could include a CO dissociation step followed by a fast decomposition of the resulting solvent adduct  $\text{Cp}(\text{CO})(\text{PPh}_3)\text{Mn}(\text{CH}_2\text{Cl}_2)$ .<sup>[10]</sup> However, the competitive dissociation of  $\text{PPh}_3$  (like in THF) and photochemical electron transfer from **6** to the solvent,<sup>[11]</sup> followed by degradation of  $\text{Mp}(\text{CH}_2\text{Cl}_2)$ <sup>[12]</sup> and **6**<sup>+</sup>, respectively, could also be implicated in the demetalation process.

Application of the most effective  $\text{CH}_2\text{Cl}_2$  demetalation protocol to the diphosphine complex **4aa** appeared to be disappointingly sluggish, giving **5aa** in low yield after prolonged irradiation time. We ascribe the drastic difference in behavior between **4aa** and **6** to the primary transformation of the former into a mixture of chelate diphosphine complexes  $\text{Cp}(\text{CO})\text{Mn}(\kappa^2\text{-PPh}_2\text{CHMePPh}_2)$  (see the Supporting information), undergoing demetalation with low rate and chemoselectivity. To our delight, in situ treatment of **4aa** with borane or acid providing protection of the pendant phosphine moiety toward coordination, allowed a rapid and nominal liberation of **5aa**. Finally, **5ab** could also be quantitatively liberated from the isolated  $[\mathbf{4ab-H}]\text{BF}_4$  upon irradiation, without any additive.

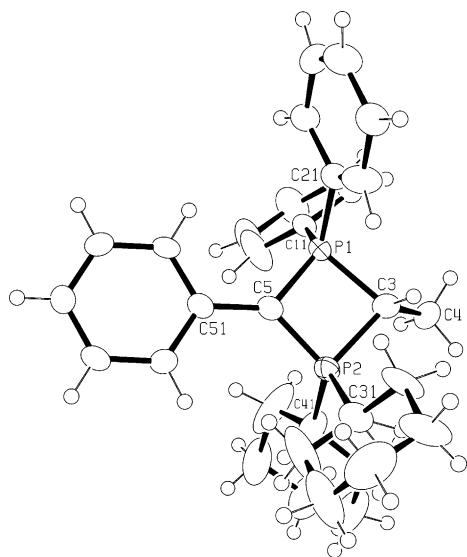
The overall two-step preparation of **5aa** and **5ab** highlights a novel unconventional route to backbone-substituted diphosphinomethanes<sup>[13]</sup> from simple and readily available building blocks,<sup>[14]</sup> which could complement the set of traditional synthetic methods for this type of ligands in terms of simplicity and modularity.

Beyond the utilization of simple secondary phosphines, we were prompted to extend the scope of this coupling process



**Scheme 2.** Coupling of carbyne complex  $[1^{\text{Ph}}]\text{BPh}_4$  with tertiary diphosphines ( $\text{BPh}_4^-$  anions omitted for clarity).

to tertiary diphosphines, in an intramolecular manner, first using dppm as a model substrate (see Scheme 2).<sup>[15]</sup> The reaction of phenylcarbyne  $[1^{\text{Ph}}]\text{BPh}_4$  with dppm was found to proceed at  $-80^{\circ}\text{C}$  in  $\text{CH}_2\text{Cl}_2$  to give a red solution of the thermally unstable intermediate  $[7]\text{BPh}_4$ , which underwent a spontaneous demetalation above  $-20^{\circ}\text{C}$  producing insoluble brown manganese decomposition products and a yellow solution of the cationic cyclic semi-ylide  $[8]\text{BPh}_4$ , isolated in 83% yield as a solvate with one  $\text{CHCl}_3$  molecule. Following the same protocol and now using our newly prepared diphosphine **5ab** (Scheme 1), the unsymmetrical cyclic semi-ylide  $[8\text{ab}]\text{BPh}_4$ , finally constructed in a fully controlled and highly convergent manner from two different carbynes and two different secondary phosphine moieties, was obtained in 90% yield. Both compounds were fully characterized, including single-crystal XRD (see Figure 2 for  $[8\text{ab}]\text{BPh}_4$  and Figure 30S in the Supporting information for  $[8]\text{BPh}_4 \cdot \text{CHCl}_3$ ).



**Figure 2.** A perspective view of  $[8\text{ab}]\text{BPh}_4$  (ellipsoids at the 30% probability level,  $\text{BPh}_4^-$  anion is not shown).

In conclusion, we have demonstrated that readily available electrophilic manganese carbyne complexes<sup>[14]</sup> can serve as stoichiometric carbyne synthons being potentially useful for organophosphorus chemistry.<sup>[16]</sup> We are now exploring the application scope of such carbyne/phosphine/phosphine coupling processes and its possible development in asymmetric version.

## Acknowledgements

Financial support from CNRS and the PICS grant 4873 (CNRS)/09-03-91060 (RFBR) is gratefully acknowledged. D. A. V. thanks CNRS for a temporary researcher position.

**Keywords:** carbyne complexes · demetalation · diphosphines · phosphoniocarbene complexes · phosphorus ylides

- [1] For the trapping of carbyne complexes with external phosphines, see: a) F. R. Kreissl, P. Stückler, *J. Organomet. Chem.* **1976**, *110*, C9–C11; b) F. R. Kreissl, P. Stückler, E. W. Meineke, *Chem. Ber.* **1977**, *110*, 3040–3045; c) A. C. Filippou, D. Wissner, G. Kociok-Köhn, I. Hinz, *J. Organomet. Chem.* **1997**, *541*, 333–343; d) D. A. Valyaev, N. Lughan, G. Lavigne, N. A. Ustyryuk, *Organometallics* **2008**, *27*, 5180–5183; e) D. A. Valyaev, N. Lughan, G. Lavigne, N. A. Ustyryuk, *Organometallics* **2011**, *30*, 2318–2332.
- [2] For intramolecular migration of metal-coordinated phosphine to the carbyne ligand, see: a) P. E. Romero, W. E. Piers, R. McDonald, *Angew. Chem.* **2004**, *116*, 6287–6291; *Angew. Chem. Int. Ed.* **2004**, *43*, 6161–6165; b) P. E. Romero, W. E. Piers, *J. Am. Chem. Soc.* **2007**, *129*, 1698–1704; c) M. L. Macnaughtan, M. J. A. Johnson, J. W. Kampf, *J. Am. Chem. Soc.* **2007**, *129*, 7708–7709; d) E. M. Leitao, E. F. van der Eide, P. E. Romero, W. E. Piers, R. McDonald, *J. Am. Chem. Soc.* **2010**, *132*, 2784–2794.
- [3] For selected studies of olefin metathesis mechanism using ruthenium phosphonocarbenes, see: a) E. F. van der Eide, W. E. Piers, *Nat. Chem.* **2010**, *2*, 571–576; b) A. G. Wenzel, G. Blake, D. G. VanderVelde, R. H. Grubbs, *J. Am. Chem. Soc.* **2011**, *133*, 6429–6439.
- [4] The only known examples to date deal with reactions of chromium and manganese carbyne complexes with excess of strongly nucleophilic  $\text{PM}_3$ , see: W. Uedelhoven, K. Eberl, W. Siebert, F. R. Kreissl, *J. Organomet. Chem.* **1982**, *236*, 301–307.
- [5] Rhenium analogue of  $[3\text{aa}]\text{BCl}_4$ :  $[\text{Cp}(\text{CO})_2\text{Re}^-\text{C}(\text{Ph})(^+\text{PM}_3)]\text{BCl}_4$  was isolated in pure state and fully characterized, see: F. R. Kreissl, K. Eberl, P. Stückler, *Angew. Chem.* **1977**, *89*, 657–658; *Angew. Chem. Int. Ed. Engl.* **1977**, *16*, 654–655.
- [6] For proton-transfer processes in closely related phosphonium betaine-type compounds probably implicating manganese *cis*-hydride species, see: a) Y. Ortin, N. Lughan, R. Mathieu, *Dalton Trans.* **2005**, 1620–1636; b) S. Sentets, R. Serres, Y. Ortin, N. Lughan, G. Lavigne, *Organometallics* **2008**, *27*, 2078–2091; c) V. V. Krivikh, D. A. Valyaev, K. I. Utegenov, A. M. Mazhuga, E. S. Tait, O. V. Semeikin, P. V. Petrovskii, I. A. Godovikov, I. V. Glukhov, N. A. Ustyryuk, *Eur. J. Inorg. Chem.* **2011**, 201–211; d) K. I. Utegenov, V. V. Krivikh, I. V. Glukhov, P. V. Petrovskii, N. A. Ustyryuk, *J. Organomet. Chem.* **2011**, *696*, 3408–3414.
- [7] CCDC-957227 (**4ab**), CCDC-957228 ( $[8]\text{BPh}_4 \cdot \text{CHCl}_3$ ), and CCDC-957229 ( $[8\text{ab}]\text{BPh}_4$ ) 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](http://www.ccdc.cam.ac.uk/data_request/cif)
- [8] a) G. Jaouen, S. Top, A. Vessières, R. Alberto, *J. Organomet. Chem.* **2000**, *600*, 23–36; b) S. Top, E. B. Kaloun, S. Toppi, A. Herrbach, M. J. McGleanchy, G. Jaouen, *Organometallics* **2001**, *20*, 4554–4561; c) L. N. Telegina, M. G. Ezernitskaya, I. A. Godovikov, K. K. Babievskii, B. V. Lokshin, T. V. Strelkova, Yu. A. Borisov, N. M. Loim, *Eur. J. Inorg. Chem.* **2009**, 3636–3643; d) J. W. Kee, Y. Y. Tan, B. H. G. Swennenhuis, A. A. Bengali, W. Y. Fan, *Organometallics* **2011**, *30*, 2154–2159.
- [9] Bulk photolysis of structurally closed ( $\eta^5\text{-C}_5\text{H}_4\text{Me}\text{Mn}(\text{CO})_2(\text{PPPh}_3)$ ) by visible light in hexane leads to a selective CO ligand substitution, see: G. Teixeira, T. Avilés, A. R. Dias, F. Pina, *J. Organomet. Chem.* **1988**, *353*, 83–91. However TRIR studies of this complex revealed the dissociation of both CO and  $\text{PPPh}_3$  ligands upon UV photolysis in heptane or supercritical  $\text{CO}_2$  solutions, see: a) J. A. Banister, M. W. George, S. Grubert, S. M. Howdle, M. Jobling, F. P. A. Johnson, S. L. Morrison, M. Poliakoff, U. Schubert, J. R. Westwell, *J. Organomet. Chem.* **1994**, *484*, 129–135; b) M. Batool, T. A. Martin, M. A. Naser, M. W. George, S. A. Macgregor, M. F. Mahon, M. K. Whittlesey, *Chem. Commun.* **2011**, *47*, 11225–11227.

- [10] The early formation of  $\text{Cp}(\text{CO})\text{Mn}(\text{PPh}_3)_2$  was observed upon photolysis of **6** in  $\text{CH}_2\text{Cl}_2$  showing CO photolability in this solvent (see the Supporting information).
- [11] The photooxidation of some organometallic compounds containing Cp and/or CO and/or  $\text{PR}_3$  ligands in chlorinated solvents ( $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ ,  $\text{CCl}_4$ ) is well documented, see for representative examples: a) O. Travesso, F. Scandola, *Inorg. Chim. Acta* **1970**, *4*, 493–498; b) C. R. Bock, M. S. Wrighton, *Inorg. Chem.* **1977**, *16*, 1309–1313; c) C. J. Leep, K. B. Kingsbury, L. McElwee-White, *J. Am. Chem. Soc.* **1988**, *110*, 7535–7536; d) J. D. Carter, K. B. Kingsbury, A. Wilde, T. K. Schoch, C. J. Leep, E. K. Pham, L. McElwee-White, *J. Am. Chem. Soc.* **1991**, *113*, 2947–2954; e) A. D. Main, L. McElwee-White, *J. Am. Chem. Soc.* **1997**, *119*, 4551–4552.
- [12] a) P.-F. Yang, G. K. Yang, *J. Am. Chem. Soc.* **1992**, *114*, 6937–6938; b) A. A. Bengali, W. Y. Fan, *Organometallics* **2008**, *27*, 5488–5493.
- [13] Compound **5aa** was prepared from  $\text{Ph}_2\text{PLi}$  and 1,1-dichloroethane in 80% yield, see: C.-L. Lee, Y.-P. Yang, S. J. Rettig, B. R. James, D. A. Nelson, M. A. Lilga, *Organometallics* **1986**, *5*, 2220–2228. Non-substituted analogue of **5ab** -  $\text{Ph}_2\text{PCH}_2\text{PCy}_2$  was prepared in 75% yield by the reaction of  $\text{Ph}_2\text{PCH}_2\text{Li}$  with  $\text{Cy}_2\text{PCl}$ , see: T. E. Wolff, L. P. Kleemann, *Organometallics* **1982**, *1*, 1667–1670.
- [14] For the preparation of manganese carbyne complexes deriving from industrially produced  $\text{Mp}(\text{CO})$ , see: E. O. Fischer, G. Besl, F. R. Kreissl in *Synthetic Methods of Organometallic and Inorganic Chemistry*, Vol. 7, (Ed.: W. A. Herrmann), George Thieme, Stuttgart, **1997**, pp. 208–209 and the Ref. [1e].
- [15] A transition-metal-templated synthesis of acyclic semi-ylides and carbodiphosphoranes from dppm and  $\text{CS}_2$  was recently reported: a) S. Stallinger, C. Reitsamer, W. Schuh, H. Kopacka, K. Wurst, P. Peringer, *Chem. Commun.* **2007**, 510–512; b) C. Reitsamer, S. Stallinger, W. Schuh, H. Kopacka, K. Wurst, D. Obendorf, P. Peringer, *Dalton Trans.* **2012**, *41*, 3503–3514.
- [16] During the last decade nucleophilic carbyne (alkylidyne) complexes were shown to be excellent homogeneous catalysts in highly challenging alkyne metathesis processes. For a recent comprehensive review on their application, see: A. Fürstner, *Angew. Chem.* **2013**, *125*, 2860–2887; *Angew. Chem. Int. Ed.* **2013**, *52*, 2794–2819.

---

Received: October 30, 2013

Published online on January 30, 2014

---