Hybrid Carbenes

Imidazoline-Functionalized Diphosphines: Models for N-Heterocyclic Carbene–Diphosphinocarbene Coupling**

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N-Heterocyclic carbenes **I** derived from imidazol-2-ylidene, also referred to as Arduengo carbenes, are important compounds whose isolation as stable, free molecules has greatly contributed to the development of carbene chemistry in recent years.[1] They show no tendency to dimerize to afford tetraazafulvalenes **II**, except under special circumstances,[2] unlike the corresponding saturated N-heterocyclic carbenes. In contrast, related diphosphinocarbenes **III** are not isolable, and have been reported in the literature only as transient species,[3,4] whereas their corresponding dimers **IV** are known to be stable.[5] As far as we are aware, no example of coupling of both types of carbenes (**V** in Figure 1) has been described.

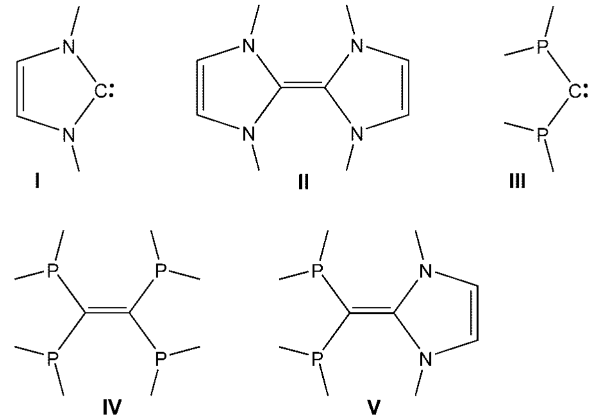
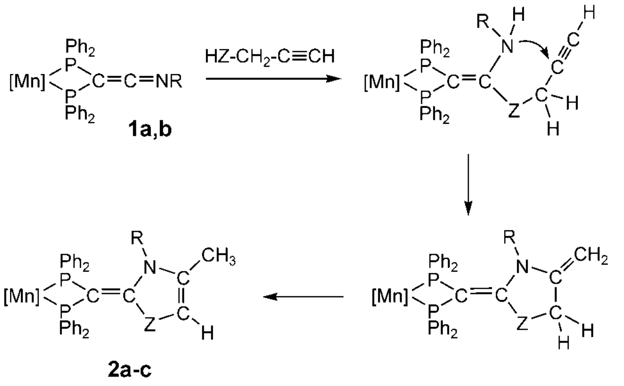


Figure 1. Schematic representation of imidazol-2-ylidenes and diphosphinylcarbenes, and their coupling products.

We report here the metal-assisted synthesis of new diphosphine ligands bearing an imidazoline residue that can serve as models of N-heterocyclic carbene–diphosphinocarbene coupling. The synthesis of analogous oxazoline-functionalized diphosphines is also described.

The diphosphinoketenimine ligand coordinated in the cationic complex $[Mn(CO)_4\{(PPh_2)_2C{=}C{=}NPh\}]^+$ (**1a**)[6] reacts with propargylamine in refluxing toluene to afford **2a** (Scheme 1), which is a diphosphine complex containing an imidazoline functionality. This complex is formed in a cycloaddition process involving the ketenimine fragment of the ligand. This result is in sharp contrast to the reaction of free diphosphinoketenimines with propargylamines, which affords phosphinine derivatives due to the additional involvement of a phosphorus atom in the cycloaddition process.[7] As proposed in Scheme 1, a likely mechanism for the formation of **2a** implies, in a first step, nucleophilic attack of the amine to the ketenimine to afford an enediamine derivative. Then, a 5-*exo*-dig addition of the phenylamino moiety to the alkyne leads to the formation of an imidazolidine cycle, which is converted into the corresponding imidazoline residue by a 1,3 proton shift from the endocyclic methylene group to the exocyclic one. This results in a change of the C=C bond position and the formation of a conjugated six-π-electron system. The reaction of **1a** with propargyl alcohol proceeds similarly to give the corresponding diphosphine complex **2b** bearing an oxazoline functionality (Scheme 1).



Scheme 1. Proposed mechanism for the formation of complexes **2a**–**c**. $[Mn] = [Mn(CO)_4]^+$. **1a**: R = Ph; **1b**: R = *p*-tolyl. **2a**: R = Ph, Z = NH; **2b**: R = Ph, Z = O; **2c**: R = *p*-tolyl, Z = NMe.

It is well known that the reaction of ketenimines with amines and alcohols usually gives the corresponding amidine and imidate derivatives, respectively.[8] However, as far as we are aware, no reaction of organic ketenimines with propargylic amines or alcohols has been reported thus far. The reaction described here therefore represents a completely new method for the formation of imidazoline and oxazoline functionalities by a new cyclization process.

The spectroscopic data of **2a**,**b** (see the Experimental Section) are in agreement with the proposed formulation. Moreover, their solid-state structures were confirmed by X-ray analysis (Figure 2 and Figure 3).[9] The most important feature in the structures of **2a** and **2b** is the presence of the imidazoline and oxazoline cycle, respectively, which is coplanar with the PCP skeleton of the diphosphane. The C1−C2 bond lengths in **2a** (1.429(4) Å) and **2b** (1.385(6) Å) are, to varying degrees, intermediate between single and double bonds, as are the P1−C1 and P2−C1 distances and the

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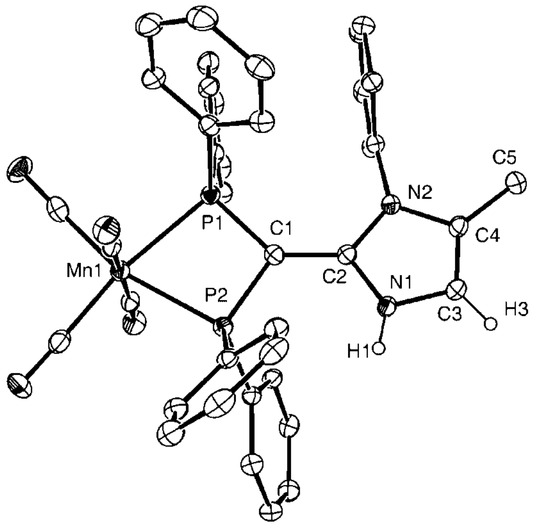

Figure 2. A view of the structure of the cation of **2a**. Selected bond lengths [Å] and angles [°]: P1-C1 1.749(3), P2-C1 1.761(3), C1-C2 1.429(4), N1-C2 1.342(3), N1-C3 1.382(4), N2-C2 1.371(3), N2-C4 1.416(3), C3-C4 1.333(4); P1-Mn-P2 69.84(2), P1-C1-P2 99.23(13), N1-C2-N2 105.4(2), N1-C2-C1 125.0(2), N2-C2-C1 129.5(2).

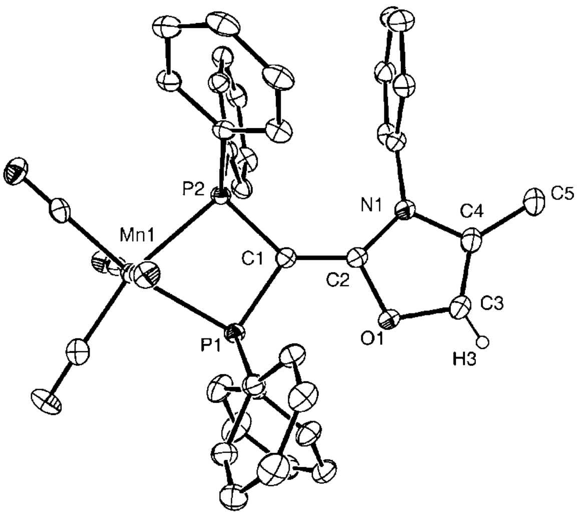

Figure 3. A view of the structure of the cation of **2b**. Selected bond lengths [Å] and angles [°]: P1-C1 1.781(4), P2-C1 1.770(4), C1-C2 1.385(6), N1-C2 1.338(6), N1-C4 1.422(5), O1-C2 1.364(5), O1-C3 1.398(6), C3-C4 1.335(7); P1-Mn-P2 71.09(4), P1-C1-P2 99.7(2), N1-C2-O1 107.9(3), N1-C2-C1 135.4(4), O1-C2-C1 116.7(4).

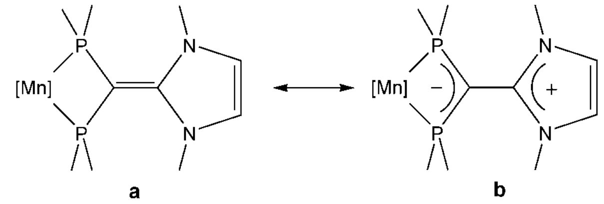

Figure 4. Resonance structures of imidazoline-functionalized diphosphane complexes. [Mn] = [Mn(CO)$_4$]$^+$.

different interatomic distances in the imidazoline and oxazoline cycles (see the legends for Figure 2 and Figure 3). These data are consistent with a bond description in the diphosphine ligand resulting from the contribution of two resonance structures, as illustrated in Figure 4 for the imidazoline case (olefinic form **a** and imidazolium ylide form **b**). Obviously, in the ylidic form the negative charge of the diphosphinomethanide fragment is stabilized by charge delocalization through the metallacycle, whereas the positive one is stabilized by π-donation from the nitrogen lone-pairs. If we consider complexes **2a** and **2b** as models for carbene–carbene coupling, the structural data described here are in agreement with the well-known nucleophilic character of N-heterocyclic carbenes[10] and the electrophilic character of transient metalladiphosphinocarbenes,[11] whose coupling should lead to a net charge-transfer from the former to the latter, thus justifying the contribution of structure **b** in Figure 4. The IR spectra of **2a** and **2b** in the $\nu_{\rm CO}$ region (see the Experimental Section), which show absorptions at values intermediate between those of diphosphine complexes and diphosphinomethanide derivatives,[12] support the above interpretation and indicate that the new diphosphines are strongly basic. Note that these absorptions occur at lower frequency in **2a** than in **2b**. This reflects the fact that the imidazoline fragment is a better electron donor than the oxazoline fragment, which also explains why the C1−C2 bond in **2b** is shorter than that in **2a**.

The ^{31}P{^{1}H} NMR spectra of **2a**,**b** at room temperature in CD$_2$Cl$_2$ show a single resonance, which suggests free rotation around the C1−C2 bond. For **2a**, this single signal is maintained when the spectrum is recorded at −80 °C, whereas it splits into two resonances, corresponding to the two inequivalent phosphorus atoms, in the case of **2b**. This observation agrees with the proposal outlined above that C1−C2 bond in **2b** has higher multiple-bond character than in **2a**.

Substituted propargylamine also reacts with coordinated diphosphinoketenimines in a similar manner. Thus, reaction of [Mn(CO)$_4${(PPh$_2$)$_2$C=C=*N*-*p*-tolyl}]$^+$ (**1b**) with methylpropargylamine affords **2c** (Scheme 1), whose spectroscopic data are similar to those of **2a**. However, the structural data derived from the X-ray analysis (Figure 5) show appreciable changes that deserve comment. Thus, the plane of the imidazoline ring in **2c** is orthogonal to the PCP plane, with the methyl substituent of the nitrogen atom apparently locked between two phenyl groups of different phosphorus atoms. Consequently, the C1−C2 bond in **2c** (1.461(9) Å) is clearly longer than in **2a** (1.429(4) Å) and **2b** (1.385(6) Å), which suggests that the imidazolium ylide resonance form is dominant for **2c**.

The structural and spectroscopic data of complexes **2a**–**c** discussed above allow us to conclude that the degree of charge transfer from the five-membered heterocycle to the metallacycle through the C1−C2 bond, and therefore the basicity of the new diphosphines, can be modulated by changing either the heteroatoms in the cycle (imidazoline or oxazoline), the substituents at these heteroatoms, or the extent of molecular motion around the C1−C2 bond.

To summarize, we have described a new cycloaddition reaction for the formation of imidazoline and oxazoline functionalities, which consists of the treatment of coordinated

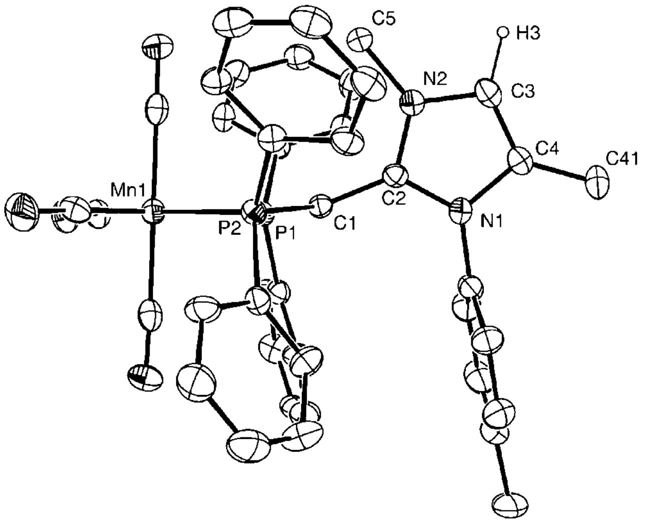

Figure 5. A view of the structure of the cation of **2c**. Selected bond lengths [Å] and angles [°]: P1-C1 1.755(7), P2-C1 1.744(7), C1-C2 1.461(9), N1-C2 1.351(8), N1-C4 1.404(9), N2-C2 1.346(8), N2-C3 1.385(9), C3-C4 1.356(9); P1-Mn-P2 69.90(7), P1-C1-P2 99.9(), N1-C2-N2 105.9(6), N2-C2-C1 124.9(6), N1-C2-C1 129.2(6).

diphosphinoketenimines with propargylamines or propargyl alcohol. The resulting functionalized diphosphine ligands can be considered as models for the coupling of either N-heterocyclic carbenes or N,O-heterocyclic carbenes with diphosphinocarbenes. These models raise the experimental challenge of coupling imidazol-2-ylidenes (Arduengo-type carbenes) with phosphinocarbenes (Bertrand-type carbenes) to yield new types of electron-rich olefins, which should behave as strongly basic phosphines.

Experimental Section

All reactions and manipulations were performed under an atmosphere of dry nitrogen by using standard Schlenk techniques. Solvents were distilled from appropriate drying agents under dry nitrogen prior to use. Chemical shifts of the NMR spectra are referenced to internal $SiMe_4$ (^1H and ^{13}C) or external H_3PO_4 (^{31}P).

2a·ClO_4: $[Mn(CO)_4\{(PPh_2)_2C{=}C{=}NPh\}]ClO_4$ (**1a**·ClO_4; 0.05 g, 0.066 mmol) was dissolved in 20 mL of toluene, and $NH_2CH_2C{\equiv}CH$ (10 μL, 0.13 mmol) was added to this solution. The mixture was then refluxed for 30 min. Cooling the solution to room temperature led to the formation of yellow crystals that were suitable for X-ray analysis. Yield: 0.04 g, 76%. Elemental analysis (%) calcd for $C_{39}H_{30}ClMnN_2O_8P_2$: C 58.04, H 3.75, N 3.47; found: C 57.87, H 4.03, N 3.53; IR (CH_2Cl_2): $\tilde{\nu} = 2081$(s), 2009 (sh), 1999 (vs), 1979 (s) cm^{-1}. ^1H NMR (300 MHz, CD_2Cl_2): $\delta = 8.28$ (s, 1H, NH), 7.8–6.6 (m, 26H, Ph + =CH), 1.60 (s, 3H, CH_3) ppm; $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): $\delta = 3.7$ (br) ppm.

2b·ClO_4: $HOCH_2C{\equiv}CH$ (20 μL, 0.33 mmol) was added to a solution of **1a**·ClO_4 (0.05 g, 0.066 mmol) in 10 mL of toluene. The mixture was then refluxed for 15 min. A solid precipitated out of the solution upon cooling, which was isolated and dried under vacuum. Crystals suitable for X-ray analysis were obtained from a mixture of $CHCl_3$ and hexane (1:1.5). Yield: 0.03 g, 57%. Elemental analysis (%) calcd for $C_{39}H_{29}ClMnNO_9P_2$: C 57.97, H 3.62, N 1.73; found: C 57.75, H 3.62, N, 1.58; IR (CH_2Cl_2): $\tilde{\nu} = 2083$ (s), 2014 (s), 2001 (vs), 1985 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 6.6$–8.0 (m, 26H, Ph + =CH), 1.26 (s, 3H, CH_3) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, CH_2Cl_2/D_2O): $\delta = 8.1$ (s, CH_3), 50.4 (t, $^1J_{C,P} = 47$ Hz, P_2C), 156.8 (s, OCN), 212.3 (br, 4 × CO) ppm; $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): $\delta = 8.7$ (br) ppm.

2c·ClO_4: $NH(CH_3)CH_2C{\equiv}CH$ (13 μL, 0.16 mmol) was added to a solution of $[Mn(CO)_4\{(PPh_2)_2C{=}C{=}N\text{-}p\text{-tolyl}\}]ClO_4$ (**1b**·ClO_4; 0.10 g, 0.13 mmol) in 40 mL of toluene. The mixture was then refluxed for 50 min. A solid precipitated out of the solution on cooling, which was isolated and dried under vacuum. Crystals suitable for an X-ray diffraction study were obtained from crystallization from a $CHCl_3$/hexane mixture (1:1.5). Yield: 0.09 g, 83%. Elemental analysis (%) calcd for $C_{41}H_{34}ClMnN_2O_8P_2$: C 58.97, H 4.10, N 3.35; found: C 59.09, H 4.08, N 3.58; IR (CH_2Cl_2): $\tilde{\nu} = 2079$ (s), 2010 (m), 1990 (vs) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.6$–6.9 (m, 24H, Ph), 2.63 (s, 3H, NCH_3), 2.22 (s, 3H, $PhCH_3$), 1.91 (s, 3H, CH_3) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, CH_2Cl_2/D_2O): $\delta = 11.7$ (s, CH_3), 22.3 (s, $PhCH_3$), 27.7 (t, $^1J_{C,P} = 45$ Hz, P_2C), 35.6 (s, NCH_3), 213 (s, 4 × CO) ppm; $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): $\delta = 16.1$ (br) ppm.

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[9] Crystal data for **2a**·ClO_4 ($C_{39}H_{30}ClMnN_2O_8P_2$): $M_r = 806.98$, monoclinic, space group $P2_1/a$, $a = 17.3936(5)$, $b = 11.2150(3)$, $c = 19.5595(6)$ Å, $\beta = 106.637(2)°$, $V = 3655.73(18)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.466$ g cm^{-3}, $F(000) = 1656$, $Cu_{K\alpha}$ radiation ($\lambda = 1.5418$ Å), $\mu = 4.913$ mm^{-1}; crystal dimensions 0.25 × 0.12 × 0.05 mm. Data collection was performed at 120(2) K on a Nonius Kappa CCD diffractometer. The structure was solved by direct methods and refined using full-matrix least-squares techniques on F^2. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed geometrically and left riding on their parent atoms, except for H1 and H3, which were found in the difference map and refined isotropically. The final cycle of full-matrix least-squares refinement based on 6890 reflections

and 486 parameters converged to R_1 ($F^2 > 2\sigma(F^2)) = 0.0426$ and wR_2 ($F^2 > 2\sigma(F^2)) = 0.1106$. Crystal data for **2b**$\cdot$(ClO$_4$)$\cdot$CHCl$_3$ ($C_{40}H_{30}Cl_4MnNO_9P_2$): $M_r = 927.33$, triclinic, space group $P\bar{1}$, $a = 11.1996(3)$, $b = 11.9095(2)$, $c = 16.1366(3)$ Å, $\alpha = 74.9480(10)$, $\beta = 79.413(2)$, $\gamma = 74.0010(10)°$, $V = 1983.34(7)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.553$ g cm^{-3}, $F(000) = 944$, Cu$_{K\alpha}$ radiation ($\lambda = 1.5418$ Å), $\mu = 6.438$ mm^{-1}; crystal dimensions $0.32 \times 0.30 \times 0.10$ mm. Data collection was performed at 120(2) K on a Nonius Kappa CCD diffractometer. The structure was solved by direct methods and refined using full-matrix least-squares techniques on F^2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed geometrically and left riding on their parent atoms except for H3 and H1D, which were found in the difference map and refined isotropically. The final cycle of full-matrix least-squares refinement based on 7427 reflections and 523 parameters converged to R_1 ($F^2 > 2\sigma(F^2)) = 0.0727$ and $wR_2(F^2 > 2\sigma(F^2)) = 0.2075$. Crystal data for **2c**$\cdot$(ClO$_4$)$\cdot$(CHCl$_3$)$_2$ ($C_{43}H_{36}Cl_7MnN_2O_8P_2$): $M_r = 1073.77$, triclinic, space group $P\bar{1}$, $a = 11.6701(16)$, $b = 11.733(2)$, $c = 18.812(3)$ Å, $\alpha = 107.144(10)$, $\beta = 92.229(7)$, $\gamma = 99.475(10)°$, $V = 2417.3(6)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.475$ g cm^{-3}, $F(000) = 1092$, Cu$_{K\alpha}$ radiation ($\lambda = 1.5418$ Å), $\mu = 6.843$ mm^{-1}; crystal dimensions $0.17 \times 0.10 \times 0.03$ mm. Data collection was performed at 200(2) K on a Nonius Kappa CCD diffractometer. The structure was solved by direct methods and refined using full-matrix least-squares techniques on F^2. All non-hydrogen atoms were refined anisotropically except for one oxygen atom in the counteranion, which is disordered over two positions. Hydrogen atoms were placed geometrically and left riding on their parent atoms, except for H3, H7, H8, H10, and H11, which were found in the difference map and refined isotropically. The final cycle of full-matrix least-squares refinement based on 7386 reflections and 590 parameters converged to R_1 ($F^2 > 2\sigma(F^2)) = 0.0868$ and $wR_2(F^2 > 2\sigma(F^2)) = 0.2437$. CCDC-241569 (**2a**), -241570 (**2b**), and -241571 (**2c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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