

Transition-Metal-like Behavior of Main Group Elements: Ligand Exchange at a Phosphinidene

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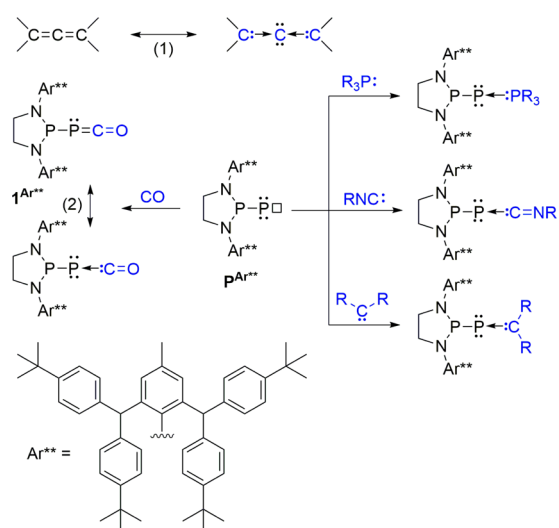
S Supporting Information

ABSTRACT: (Phosphino)phosphaketenes ($>\text{P}=\text{P}=\text{C}=\text{O}$) behave as (phosphino)phosphinidene-carbonyl adducts ($>\text{P}=\text{P}=\text{C}=\text{O}$). CO scrambling was observed using ^{13}C labeled CO, and exchange reactions with phosphines afford the corresponding (phosphino)-phosphinidene-phosphine adducts ($>\text{P}=\text{P}=\text{PR}_3$). The latter react with isonitriles and singlet carbenes giving (phosphino)phosphinidene-isonitrile ($>\text{P}=\text{P}=\text{C}=\text{NR}$) and -carbene adducts ($>\text{P}=\text{P}=\text{C}=\text{C}$). Based on experimental results and DFT calculations, it is shown that these “ligand” exchange reactions occur via an associative mechanism as classically observed with transition metal complexes.

Pioneered by Frenking, the concept of “carbones,”¹ in which an allene could be regarded as a carbon(0) atom stabilized by two Lewis bases ($\text{L}:\rightarrow\text{C}=\text{L}$),² is leading to a rethinking of the bonding in main-group element derivatives.^{3–5} This concept creates a strong analogy between transition metals and main group compounds, and indeed, during the past decade it has been shown that the latter can mimic to some extent the behavior of transition metal complexes.⁶ Similar to the latter, carbenes and their analogues feature nonbonding electrons and an accessible vacant orbital, thereby allowing for the activation of small molecules,⁷ and even the stabilization of highly reactive species.⁸ We and others have shown that CO can “coordinate” stable singlet electrophilic carbenes,⁹ and Braunschweig et al.¹⁰ were able to isolate the first main group dicarbonyl compound in the reaction of a metal–borylene with carbon monoxide. Lastly, we recently reported that the stable singlet phosphinidene $\text{P}^{\text{Ar**}}$ ^{11,12} was not only able to bind CO but also other Lewis bases such as phosphines, isonitriles, and carbenes (Scheme 1).¹³ These results prompted us to explore whether these Lewis bases act as “L ligands” for singlet phosphinidenes and therefore undergo one of the most prototypical reactions in transition metal chemistry, namely L ligand exchange.

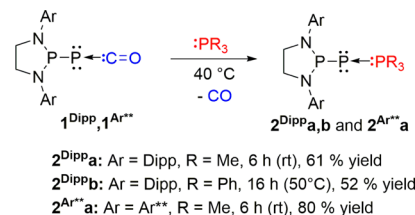
The carbonyl group is arguably one of the more labile ligands for transition metals. Therefore, we started our study by investigating whether the CO group of the phosphaketene $\mathbf{1}^{\text{Dipp}}$ could be substituted thermally by a phosphine,¹⁴ one of the most classical ligand exchange reactions in organometallic chemistry. Upon addition of trimethyl- and triphenylphosphine to phosphaketene $\mathbf{1}^{\text{Dipp}}$, we observed gas evolution (identified by ^{13}C NMR as CO; $\delta = 184.5$ ppm) and after a few

Scheme 1. “Carbone” Concept (1) and Its Extension to the Phosphaketene $\mathbf{1}^{\text{Ar**}}$ (2), and the Reactivity of the Stable Singlet Phosphinidene $\text{P}^{\text{Ar**}}$ with Lewis Bases



hours at room temperature and 50 °C, respectively, the ^{31}P NMR spectra indicated the clean formation the phosphine-phosphinidene adducts $\mathbf{2}^{\text{Dippa}}$ and $\mathbf{2}^{\text{Dippb}}$ (Scheme 2).

Scheme 2. Carbon Monoxide/Phosphine Exchange at a Phosphinidene



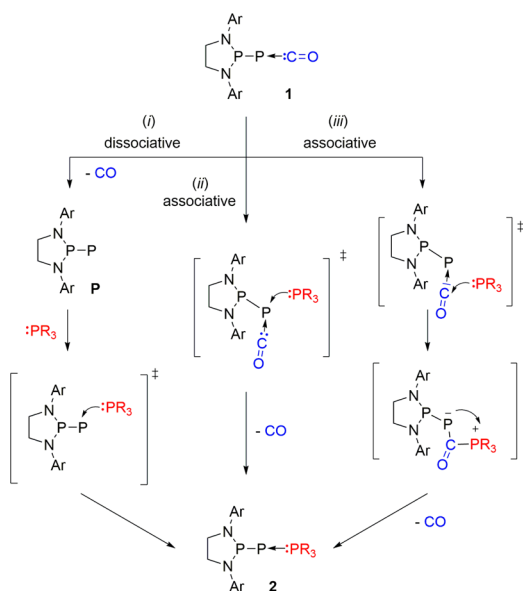
Interestingly, although the bulkier phosphaketene $\mathbf{1}^{\text{Ar**}}$ also reacted quickly with trimethylphosphine to give adduct $\mathbf{2}^{\text{Ar**a}}$, no reaction occurred with triphenylphosphine even at 60 °C and prolonged reaction times.

By analogy with transition metal chemistry, two mechanisms could be envisaged (Scheme 3): (i) a dissociative mechanism involving the formation of phosphinidene P followed by

Received: November 4, 2016

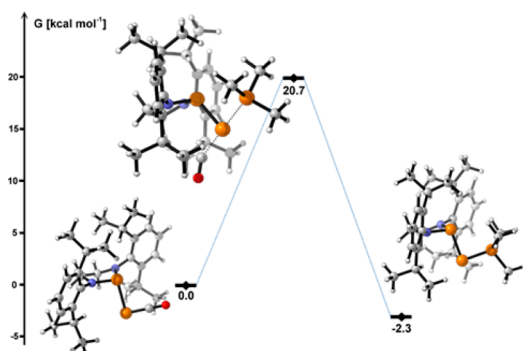
Published: November 23, 2016

Scheme 3. Possible Mechanisms for the Ligand Exchange at the Phosphinidene Center



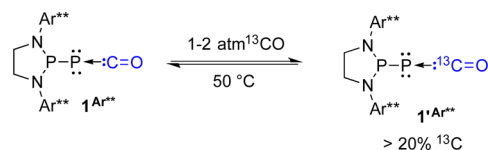
addition of the phosphine, as classically observed for 18-electron complexes; (ii) an associative mechanism in which the phosphine would attack at the phosphorus center with CO acting as a leaving group, as observed for 17-electron complexes. Additionally, another associative mechanism (iii) in which the phosphine would add onto the carbonyl group followed by decarbonylation could be considered.

We have already demonstrated that the bulky phosphinidene $\text{P}^{\text{Ar}^{**}}$ quickly reacts with triphenylphosphine, even at room temperature,¹³ and because Ph_3P does not react with $\text{1}^{\text{Ar}^{**}}$, the dissociative mechanism (i) involving P can readily be excluded. Mechanism (iii) is also unlikely since the carbonyl carbon of $\text{1}^{\text{Ar}^{**}}$ seems too far from the Ar^{**} substituents to be protected toward the triphenylphosphine, but it cannot definitely be excluded.¹⁵ For the associative mechanism (ii) we performed DFT calculations, which predict that the substitution of the CO group of 1^{Dipp} by trimethylphosphine is exergonic by 2.3 kcal mol⁻¹ with an energy barrier of 20.7 kcal mol⁻¹; note that this value is significantly lower than the barrier for the endergonic decarbonylation of 1^{Dipp} into P (31 kcal mol⁻¹). Interestingly, the transition state features a T-shape geometry in which the entering and leaving groups are 180° apart, as observed for ligand exchange in transition metal chemistry (Figure 1).

Figure 1. Energy profile and geometry of the transition state for the CO/ PMe_3 exchange.

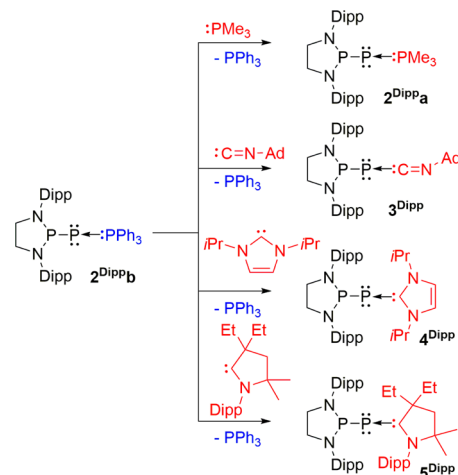
These results encouraged us to investigate the CO/CO exchange reaction (Scheme 4). A solution of phosphaketene

Scheme 4. CO/CO Exchange Reaction



$\text{1}^{\text{Ar}^{**}}$ was exposed to 1–2 atm of labeled ^{13}C O and after 2 days at 50 °C, a significant increase of the ketene-CO ^{13}C resonance (>20% based on ^{31}P NMR) was observed indicating the feasibility of CO scrambling.

To provide further evidence dismissing the associative mechanism (iii) in the CO/ PR_3 and CO/CO exchanges, we turned our attention to exchange reactions involving the phosphinidene–triphenylphosphine adduct 2^{Dippb} as a starting material. To our delight, addition at room temperature of trimethylphosphine cleanly led to the corresponding phosphinidene adduct 2^{Dippa} (Scheme 5). Note that precedents for a

Scheme 5. Exchange of PPh_3 by PMe_3 , Isonitrile, N -Heterocyclic Carbene, and CAAC Ligands

similar reaction can be found in the literature.¹⁶ More interestingly, when adamantyl isocyanide was added to 2^{Dippb} , the corresponding isonitrile adduct 3^{Dipp} was cleanly formed along with free PPh_3 after 8 h at room temperature. Using 2^{Dippa} , featuring the more basic trimethylphosphine, the same reaction also occurred but only after heating at 60 °C for 24 h. Lastly, we investigated the phosphine–carbene exchange reaction, and indeed an N -heterocyclic carbene can displace the phosphine ligand. Upon addition of 1,3-diisopropylimidazol-2-ylidene to 2^{Dippb} clean formation of adduct 4^{Dipp} and release of PPh_3 was detected over 12 h at room temperature. Furthermore, this approach is also valid for other carbenes such as a CAAC [cyclic (alkyl) (amino)carbene].¹⁷ In this case slight heating at 50 °C for 12 h leads to the clean formation of the carbene adduct 5^{Dipp} . It is important to note that adducts 4^{Dipp} / 5^{Dipp} cannot be obtained by addition of a singlet carbene to the carbonyl adduct 1^{Dipp} ; instead, an addition/rearrangement occurs.¹⁸

We performed DFT calculations at the B3LYP-D3BJ/def2-TZVP level¹⁹ of theory to understand the kinetics and

thermodynamics of the ligand exchange process (Figure 2). The phosphinidene–ligand stability follows the following

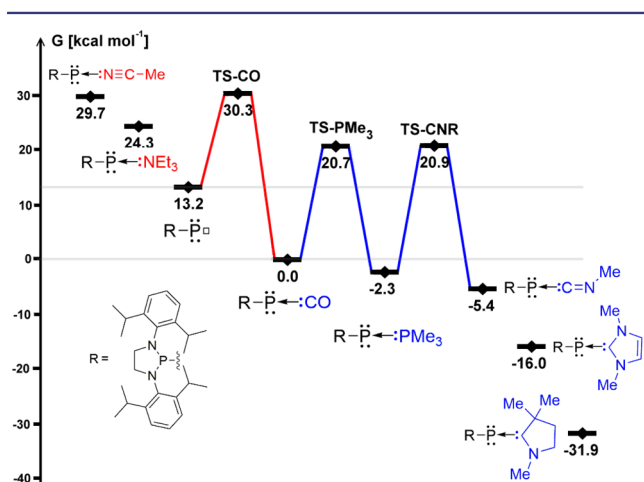


Figure 2. Energy profile for the ligand exchange reactions at a phosphinidene center.

order: $\text{CO} < \text{PR}_3 < \text{CNR} < \text{NHC} < \text{CAAC}$. Interestingly, phosphinidene adducts with amines (+24.3 kcal/mol) and nitriles (+29.7 kcal/mol) are energetically higher than the free phosphinidene (+13.2 kcal/mol) and therefore unstable toward dissociation. It is important to note that the transition state for CO/PR_3 (+20.7 kcal/mol) and PR_3/CNR exchanges (+20.9 kcal/mol) are significantly lower in energy than the decarbonylative transition state of the reaction leading to the free phosphinidene (+30.3 kcal/mol).¹³ This further confirms that the free singlet phosphinidene is not involved in these transformations.²⁰

These results demonstrate that “L ligand” exchange, the prototypical reaction for transition metal complexes, can also occur at a main group element center. We are currently investigating the scope of this concept.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b11496.

Synthesis, characterization, and computational data (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Thanks are due to the NSF (CHE-1359809) for financial support, and to the Alexander von Humboldt foundation for a Feodor-Lynen scholarship (M.M.H.). We are also grateful to the Keck Foundation for funding the KeckII computer center.

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