Manganese Complexes

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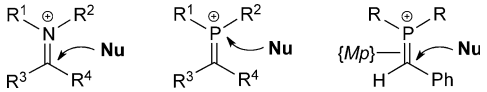
Umpolung of Methylenephosphonium Ions in Their Manganese Half-Sandwich Complexes and Application to the Synthesis of Chiral Phosphorus-Containing Ligand Scaffolds**

Dmitry A. Valyaev, Oleg A. Filippov, Noël Lugan,* Guy Lavigne, and Nikolai A. Ustynyuk*

Abstract: *Half-sandwich manganese methylenephosphonium complexes $[Cp(CO)_2Mn(\eta^2\text{-}R_2P{=}C(H)Ph)]BF_4$ were obtained in high yield through a straightforward reaction sequence involving a classical Fischer-type manganese complex and a secondary phosphine as key starting materials. The addition of various nucleophiles (Nu) to these species took place regioselectively at the double-bonded carbon center of the coordinated methylenephosphonium ligand $R_2P^+{=}C(H)Ph$ to produce the corresponding chiral phosphine complexes $[Cp(CO)_2Mn(\kappa^1\text{-}R_2P{-}C(H)(Ph)Nu)]$, from which the phosphines were ultimately recovered as free entities upon simple irradiation with visible light. The synthetic potential of this umpolung approach is illustrated herein by the preparation of novel chiral pincer-type phosphine–NHC–phosphine ligand architectures.*

Iminium salts are of utmost importance in organic synthesis,[1] owing in particular to their key role as intermediates in many enantioselective organocatalytic transformations of carbonyl compounds.[2] However, the synthetic utility of their phosphorus analogues, methylenephosphonium ions,[3,4] remains limited to a few examples of [2+2][4h,j] and [2+4][4b,e,g] cycloaddition, the ene reaction,[4b,e] electrocyclic cyclization with an arene ring,[4e,f] stereoselective rearrangement to give phosphaalkenes,[4d] and the phospha-Stork reaction.[4l] Whereas the reactivity of iminium salts is governed by the strong electrophilicity of the carbon atom (Scheme 1), the methylenephosphonium salts undergo regioselective addition of nucleophiles (Nu = F^-, Cl^-, and MeO^-)[3a,b,4a] at the electropositive phosphorus center (Scheme 1). In attempts to explore the reactivity of manganese methylenephosphonium complexes $[Cp(CO)_2Mn(\eta^2\text{-}R_2P{=}C(H)Ph)]BF_4$, readily available from half-sandwich Mn^I Fischer carbenes and secondary phosphines as key starting materials, we observed that the coordinated methylenephosphonium moiety undergoes regioselective addition of nucleophiles at the carbon center, thus mimicking the reactivity mode of iminium salts (Scheme 1; in this scheme and thereafter $\{Mp\} = Cp(CO)_2Mn$). This key observation inspired the development of an unconventional synthetic methodology toward a wide variety of organophosphorous derivatives, as illustrated herein by a simple route to a novel family of chiral pincer-type phosphine–NHC–phosphine ligands (NHC = N-heterocyclic carbene).



Scheme 1. Respective regioselectivities observed in the addition of nucleophiles to iminium (left), methylenephosphonium salts (center), and manganese methylenephosphonium complexes (right, $\{Mp\} = CpMn(CO)_2$).

Earlier investigations in our laboratories had previously established that the cationic manganese carbyne $[\{Mp\}^+{\equiv}C{-}Ph]BPh_4$ ($[\mathbf{2}]BPh_4$) reacts sequentially with diphenylphosphine and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to give the η^1-phosphinocarbene complex **3a**, which undergoes facile CO insertion to form the η^3-phosphinoketene complex **4a** (see structures in Scheme 2).[5] We have now found that further protonation of **4a** with $HBF_4{\cdot}OEt_2$ leads to the quantitative formation of the cationic complex $[\mathbf{5a}]^+$ with a η^2-methylenephosphonium ligand (Scheme 2).[6,7] This reaction is a rare example of controlled CO deinsertion from a ketene ligand in a mononuclear complex, a reaction previously only explicitly induced by chloride abstraction within the complex $[(t\mathrm{Bu}_2\mathrm{PCH}_2P t\mathrm{Bu}_2)(Cl)Ir(\eta^2\text{-}Ph_2C{=}C{=}O)]$ to afford $[(t\mathrm{Bu}_2\mathrm{PCH}_2P t\mathrm{Bu}_2)(CO)Ir{=}CPh_2]^+$.[8,9]

A DFT study of the protonation-induced CO deinsertion in **4a** with CF_3OH as a model of a strong acid revealed that the reaction occurs through the initial formation of a hydrogen-bonded adduct involving the oxygen atom of the ketene ligand, followed by proton transfer to the C_β atom with concomitant $C_\alpha{-}C_\beta$ bond cleavage to afford $[\mathbf{5a}]^+$ (see the Supporting Information for full details). The calculated TS energy of 3.8 kcal mol^{-1} (SMD method, CH_2Cl_2) is consistent with the experimental observation of a rapid transformation $\mathbf{4a} \rightarrow [\mathbf{5a}]^+$ at −80 °C.

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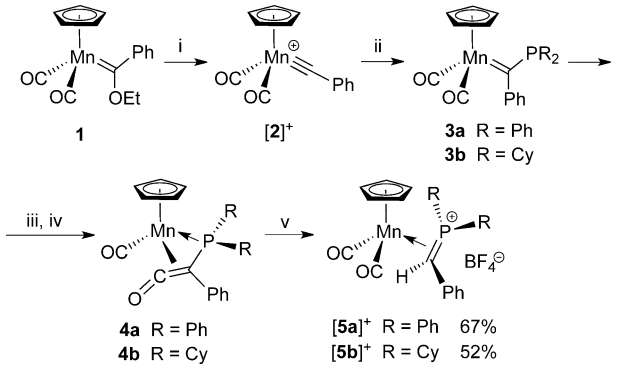


Scheme 2. Synthesis of manganese methylenephosphonium complexes $[\mathbf{5}]^+$: i) BCl_3, hexane, −80 °C; ii) $R_2PH/i Pr_2NEt$, THF, −80 °C; iii) filtration through Al_2O_3, THF, −80 °C→RT; iv) extraction 1 M aqueous NaOH/toluene, RT; v) $HBF_4{\cdot}OEt_2$, CH_2Cl_2, −80 °C→RT. Cy = cyclohexyl.

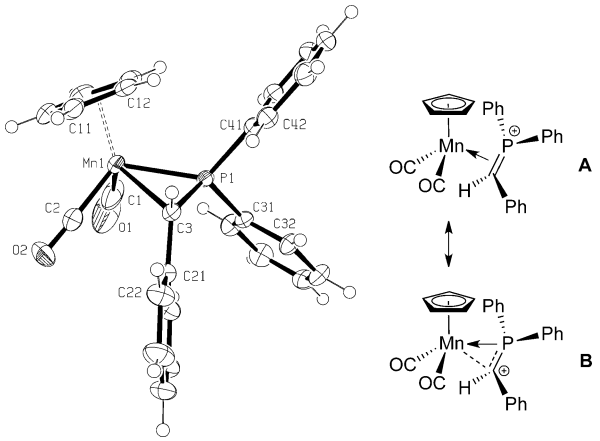
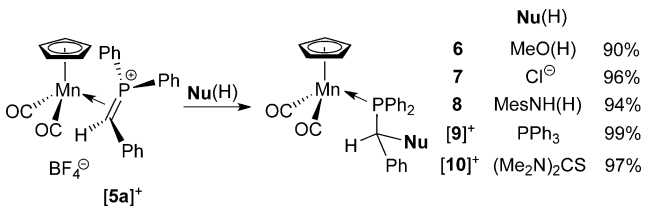


Figure 1. A perspective view of the cationic part of $[\mathbf{5a}]BF_4$ (ellipsoids shown at the 30% probability level) and proposed limiting resonance forms **A** and **B** for the bonded η^2-methylenephosphonium ligand.

Contrary to the majority of free methylenephosphonium salts, the solid methylenephosphonium complexes $[\mathbf{5}]^+$ are air-stable and almost insensitive to moisture.[10] In solution, however, they react cleanly with a variety of nucleophiles to form the corresponding manganese κ^1-phosphine complexes of the type **6**–**10** in very high yield, as illustrated for complex $[\mathbf{5a}]^+$ in Scheme 3. Notably, complex $[\mathbf{5a}]^+$ was found to



Scheme 3. Reactions of manganese complex $[\mathbf{5a}]^+$ with nucleophiles. Mes = mesityl (2,4,6-trimethylphenyl).

alkylate methanol in the absence of an added base under mild conditions (room temperature, THF, 24 h) to afford **6**. Further reactions with other nucleophiles, either anionic (Cl^-) or neutral (2,4,6-trimethylaniline, PPh_3, tetramethylthiourea), were found to take place almost instantaneously in solution in dichloromethane at room temperature. Clearly, all these complexes result from the addition of the nucleophile to the carbon atom of the η^2-methylenephosphonium moiety, thus revealing an inverse regioselectivity relative to that observed for free methylenephosphonium salts (Nu = F^-, Cl^-, and MeO^-)[3a,b,4a] and in the isolated case of a $[W(CO)_5]$ complex (Nu = BF_4^-).[11]

Looking for some clues regarding the novel reactivity pattern of manganese methylenephosphonium complexes, we performed X-ray diffraction analysis of $[\mathbf{5a}]^+$ (Figure 1).[12] The η^2-methylenephosphonium ligand in $[\mathbf{5a}]^+$ adopts the so-called horizontal coordination mode typically found in η^2-alkene complexes in particular.[13] The interatomic C–P bond distance (P1–C3 = 1.735(2) Å) within the coordinated methylenephosphonium ligand is intermediate between single and double C–P bonds, and very close to those observed in related tungsten complexes.[6] Whereas the Mn1–P1 bond distance (2.2405(7) Å) compares well with the Mn–P distance found in the archetypal phosphine complex $[Cp(CO)_2Mn(PPh_3)]$ (2.236(3) Å),[14] the Mn–C bond (Mn1–C3 = 2.257(2) Å) was found to be significantly elongated relative to those observed for η^2-alkene analogues (CCDC average length of 2.17 Å). Taken together, these structural features reflect a contribution to the structure of $[\mathbf{5a}]^+$ of the limiting resonance form **B**, in which a phosphorus lone pair pointing to the metal atom is developing along with a benzyl-type carbocation likely to be captured by incoming nucleophiles Nu(H) to afford the isolated manganese phosphine complexes **6**–**10** (Scheme 3). Although in the case of Cl^- an alternative reversible addition to the phosphorus atom in $[\mathbf{5}]^+$ to form the zwitterionic adduct $[\{Mp\}^-C(H)Ph-P^+Ph_2Cl]$ cannot be excluded within this model, the overall reaction outcome is thermodynamically controlled owing to the irreversible formation of the highly stable manganese phosphine complex **7**. For neutral nucleophiles, the initial formation of similar net cationic adducts $[\{Mp\}^-C(H)Ph-P^+Ph_2-Nu^+H]$ is even more unlikely.

With the aim to exploit the synthetic potential of complex $[\mathbf{5a}]^+$, we next focused on its large-scale preparation. Its precursor **4a** was obtained on a 20 mmol scale from the Fischer carbene **1**, Ph_2PH, and the Hünig base and was next used as the crude product in the final protonation step to afford $[\mathbf{5a}]^+$ in 67% overall yield from **1** (Scheme 2). The same procedure was successfully applied to the synthesis of complex $[\mathbf{5b}]^+$ from Cy_2PH, albeit in slightly reduced yield.

Having established an economically viable source of manganese methylenephosphonium complexes,[15] we investigated their use for the synthesis of valuable organophosphorus products. Typically, the reaction of $[\mathbf{5a}]^+$ with *N*-mesitylimidazole proceeded cleanly and almost instantaneously at room temperature in CH_2Cl_2 to give the phosphine complex $[\mathbf{11}]^+$ (Scheme 4). Further irradiation of the resulting solution with visible light in the presence of $HBF_4{\cdot}OEt_2$ according to our previously reported procedure[16] produced in 92% yield the free chiral phosphine $[\mathbf{12}]^+$ with a pendent imidazolium moiety: the possible precursor of a chelating phosphine–NHC ligand. Notably, access to this type of

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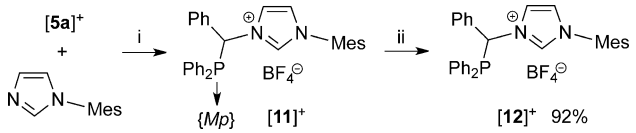


Scheme 4. Synthesis of the phosphine–NHC preligand $[\mathbf{12}]^+$: i) CH_2Cl_2, RT, 5 min; ii) visible light, $HBF_4{\cdot}OEt_2$, CH_2Cl_2, RT, 15 min, then aqueous $NaHCO_3$.

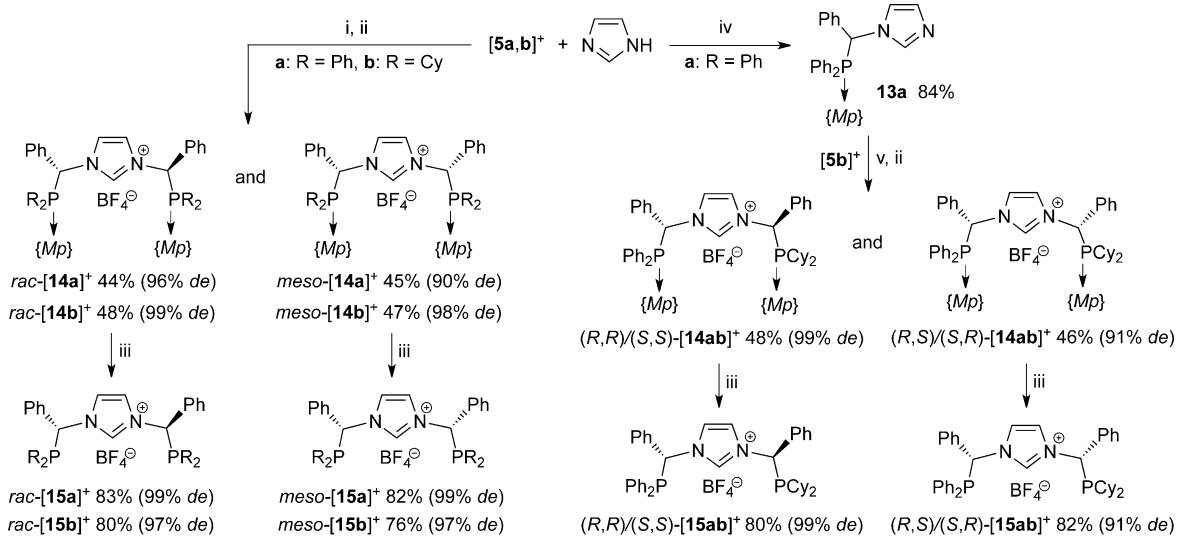
preligand even with a simple CH_2 linker between the phosphine and the imidazolium moieties would typically require a tedious multistep synthesis with a moderate overall yield.[17]

We next observed that the slow addition of one equivalent of nonsubstituted imidazole to a solution of one of the complexes $[\mathbf{5}]^+$ at room temperature resulted in the precipitation of imidazolium tetrafluoroborate along with the formation of a binuclear manganese complex $[\mathbf{14a}]^+$ or $[\mathbf{14b}]^+$ as an equimolar mixture of *rac* and *meso* isomers (Scheme 5). The {*Mp*} moiety not only stabilizes the methylenephosphonium salts and inverses the regioselectivity of the nucleophilic addition, but also acts as a phosphine protecting group and facilitates in particular the separation of the diastereoisomers of $[\mathbf{14}]^+$ by column chromatography on silica. Finally, photochemical deprotection of the diastereomerically pure complexes $[\mathbf{14}]^+$ (Scheme 5) afforded four isomeric phosphine–imidazolium products $[\mathbf{15}]^+$ in approximately 80% yield. The latter complexes are precursors to a novel family of C_2- and C_s-symmetric pincer-type phosphine–imidazolinylidene–phosphine ligands with single-carbon-atom spacer between phosphine and NHC fragments.[18] The relative configuration of the stereocenters in $[\mathbf{15}]^+$ was assigned by X-ray diffraction studies for *meso*-$[\mathbf{15a}]BF_4$ and *rac*-$[\mathbf{14b}]BF_4$ (see Figures S3 and S1, respectively).[12]

We further observed that the intermediate monoalkylated imidazole complex **13a** can be prepared in 84% yield under more statistically favorable conditions, that is, by the slow addition of a solution of $[\mathbf{5a}]^+$ to a solution containing 10 molar equivalents of imidazole (Scheme 5), thus opening up a route to the synthesis of precursors of unsymmetrical pincer-type ligands. Indeed, subsequent treatment of isolated **13a** with complex $[\mathbf{5b}]^+$, followed by chromatographic separation of the diastereoisomers, gave the complexes $[\mathbf{14a,b}]^+$ in excellent yield, one of which was characterized by X-ray diffraction (see Figure S2).[12] Photochemical deprotection under the usual conditions afforded precursors $[\mathbf{15ab}]^+$ to unsymmetrical pincer-type ligands in about 80% yield, thus illustrating the modular character of our synthetic approach (Scheme 5).

Finally, to appraise the benefits of using imidazolium compounds $[\mathbf{15}]^+$ as sources of unprecedented pincer-type ligands, we treated *rac*-$[\mathbf{15b}]^+$ with $[Rh(acac)(CO)_2]$ (acac = acetylacetonate). Monitoring of the reaction by IR spectroscopy revealed the displacement of one carbonyl ligand by the PCy_2 moiety at room temperature, followed by the clean conversion of this intermediate at 65 °C into the desired pincer complex *rac*-$[\mathbf{16}]^+$ by the action of the acetylacetonate ligand as an internal base.[19] The complex *rac*-$[\mathbf{16}]^+$ was isolated in 90% yield and fully characterized by spectroscopic methods and by X-ray diffraction (Figure 2).[12]

In conclusion, we have observed an umpolung of the methylenephosphonium cation when coordinated to a manganese center. This reactivity offers a simple route to hybrid backbone-chiral pincer-type phosphine–NHC–phosphine ligands. The adaptation of our synthetic strategy to the preparation of optically active manganese methylenephosphonium complexes and further applications of the original phosphine–NHC ligands in homogeneous catalysis are under investigation.



Scheme 5. Preparation of the pincer-type phosphine–NHC–phosphine preligands $[\mathbf{15}]^+$: i) slow addition of imidazole to $[\mathbf{5}]^+$, CH_2Cl_2, RT, 2–4 h; ii) column chromatography on silica; iii) visible light, $HBF_4{\cdot}OEt_2$, CH_2Cl_2, RT, 30–40 min, then aqueous $NaHCO_3$; iv) slow addition of $[\mathbf{5a}]^+$ to imidazole (10 equiv), CH_2Cl_2, RT, 4 h; v) $[\mathbf{5b}]^+$, CH_2Cl_2, RT, 10 min.

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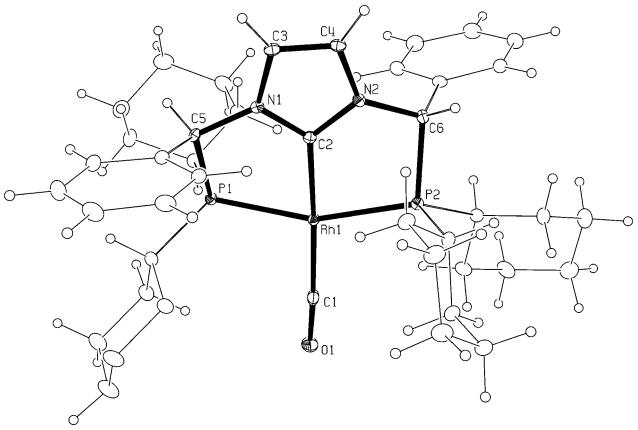

Figure 2. A perspective view of the cationic part of the rhodium pincer-type complex *rac*-[**16**]BF_4 (ellipsoids shown at the 30% probability level).

Keywords: manganese · methylenephosphonium ligands · P ligands · photochemical demetalation · pincer ligands

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Communications

Manganese Complexes

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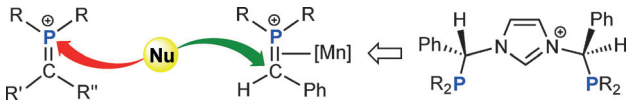
Umpolung of Methylenephosphonium Ions in Their Manganese Half-Sandwich Complexes and Application to the Synthesis of Chiral Phosphorus-Containing Ligand Scaffolds



Reactivity trend reversal: Methylenephosphonium salts coordinated to a manganese center were found to exhibit "iminium-like" reactivity towards nucleophiles (see scheme). This unprecedented umpolung enables the instant formation of carbon–heteroatom bonds, highlighted by the synthesis of novel chiral pincer-type phosphine–NHC–phosphine ligands.

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