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Transformation of a Phosphorus-Bound Cp* Moiety in the Coordination Sphere of Manganese Carbonyl Complexes

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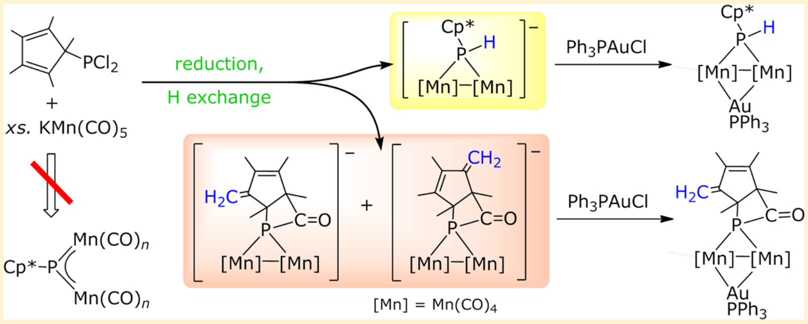
S *Supporting Information*



ABSTRACT: The reaction of Cp*PCl_2 with K[$Mn(CO)_5$] yields two novel anionic products, [$Mn_2(CO)_8(\mu\text{-}PC_{11}H_{14}O)$]$^-$ (**1**$^-$) and [$Mn_2(CO)_8(\mu$-PHCp*)]$^-$ (**2**$^-$), instead of the expected phosphinidene complexes with a delocalized Mn−P−Mn bond system. By treating these anionic complexes with [Ph_3PAuCl], they are converted into corresponding neutral derivatives [$Mn_2(CO)_8(\mu\text{-}PC_{11}H_{14}O)(\mu\text{-}AuPPh_3)$] (**3**) and [$Mn_2(CO)_8(\mu$-PHCp*)($\mu$-$AuPPh_3$)] (**4**). NMR investigations and X-ray structural analyses for **1**$^-$, **3**, and **4** show that the compounds **1**$^-$ and **3** as well as **2**$^-$ and **4** reveal similar molecular structures in which the neutral complexes **3** and **4** contain $AuPPh_3$ units bridging Mn−Mn bonds. In comparison to **1** and **3**, complexes **2** and **4** possess one additional H atom bound at the P atom. The structures of **1** and **3** include a novel bicyclic unit consisting of a C_5 ring of the former Cp* moiety conjugated to a CCC(O)P four-membered ring. The latter is built by a CO group of a former Mn carbonyl fragment connecting a P and a C atom of the cycle. One of the methyl groups of the Cp* ligand became a CH_2 unit, resulting in two isomers containing an exocyclic CH_2 moiety in the positions three or five of the C_5 ring. Both isomers were found in the reaction mixture, with one as the major isomer. The proposed reaction pathway is based on XRD, NMR, and MS data and includes the reduction of a transient [Cp*P($Mn(CO)_5)_2$] complex by [$Mn(CO)_5$]$^-$, a proton transfer from the neutral to the reduced complex, and a successive reduction of the protonated species. The neutral bicyclic compound **3**, containing a 2-phosphacyclobutanone ring, is light sensitive and decomposes to tetramethylfulvene, possibly by a radical decarbonylation mechanism via a transient phosphacyclobutane derivative, [$C_5(CH_3)_4(CH_2)P(Mn(CO)_4)_2AuPPh_3$] (**5**), detected by NMR spectroscopy.

INTRODUCTION

Carbene complexes of transition metals bearing a CR_2 unit are important compounds in organic syntheses and catalyses such as metathesis, polymerization, and oxidation of olefins.[1] Their isolobal relatives are phosphinidene complexes containing a PR unit that can be bound on up to four metal fragments. They show a high variety in coordination modes and structural features[2] and are valuable synthons for the design of organophosphorus derivatives containing low-coordinate phosphorus centers. Whereas big efforts in the reactivity of terminal phosphinidene complexes have been made,[2a,3] the class of 2-fold bridging complexes possessing a delocalized M−P−M bond is comparatively rather underdeveloped. Depending on the valence electron (VE) number of the coordinated metal fragments ML_n, the formed molecules possess no bond (type **A**, ML_n = $M(CO)_5$ (M = Cr, Mo, W), $MnCp(CO)_2$, $Fe(CO)_4$, $CpCo(CO)_2$),[4] a single bond (type **B**, ML_n = $Cp(CO)_2$ (M = M, W), $Co(CO)_3$),[5,6] a double bond (type **C**, ML_n = MoCp(CO)I,[7] $VCp(CO)_2$[8]), or a triple bond (type **D**, ML_n = MoCp(CO)[7]) between the metal centers. Rarely, they tend to dimerize and form type **E** complexes (ML_n = $Fe(CO)_3$[9]). Type **B** or **E** complexes are usually achieved if complex fragments with an odd number of VEs are used. For even-numbered complex moieties usually type **A** complexes are formed, and only by using electron-deficient fragments are the multiple-bonded species **C** and **D** observed. The delocalized 3c-4e M−P−M bond in **A** is responsible for the electron-deficient P atom and provides its strong electrophilic reactivity pattern. Thus, most commonly μ-phosphinidene complexes easily react with nucleophiles to form the addition products **F**.

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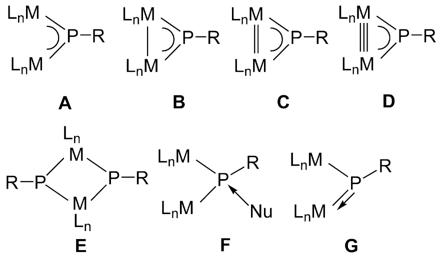


Besides the nature of the complex fragment also the properties of the substituent R at the phosphinidene P atom can decisively influence the structure and reactivity of the compounds. The Ruiz group has shown the influence of the mesityl substituent, which can move to a transition metal and act as an additional ligand, providing type **G**-like and other complexes.[7,10] A unique reaction behavior appears when the P atom bears a Cp* group. The resulting complex [Cp*P{W(CO)$_5$}$_2$][11] shows a rich subsequent chemistry, which was intensively investigated in our group. The lability and the coordination properties of the η^1-bound Cp* group[12] allow its shifting to the metal atom after thermal activation, forming an intermediate containing a phosphorus−tungsten triple bond of the formula [Cp*(CO)$_2$W≡P→(CO)$_5$].[13] This transient compound serves as a versatile precursor in reactions with unsaturated species such as alkynes,[14] phosphaalkynes,[15] and binuclear carbonyl complexes containing a metal−metal triple bond.[16] With nitriles, the μ-phosphinidene complex undergoes migration reactions of the Cp* substituent to form novel P-containing heterocycles.[17] UV radiation induces elimination of a Cp* radical to yield stable triphospha- or arsadiphosphaallyl radicals in the reaction with diphosphenes.[18] Only if MesC≡P reacts with [Cp*P{W(CO)$_5$}$_2$] a ring expansion of the Cp* substituent has been found so far,[15] and primary phosphines provoke hydrophosphination reactions to expand the Cp* moiety, yielding diphosphanorbornene derivatives.[19]

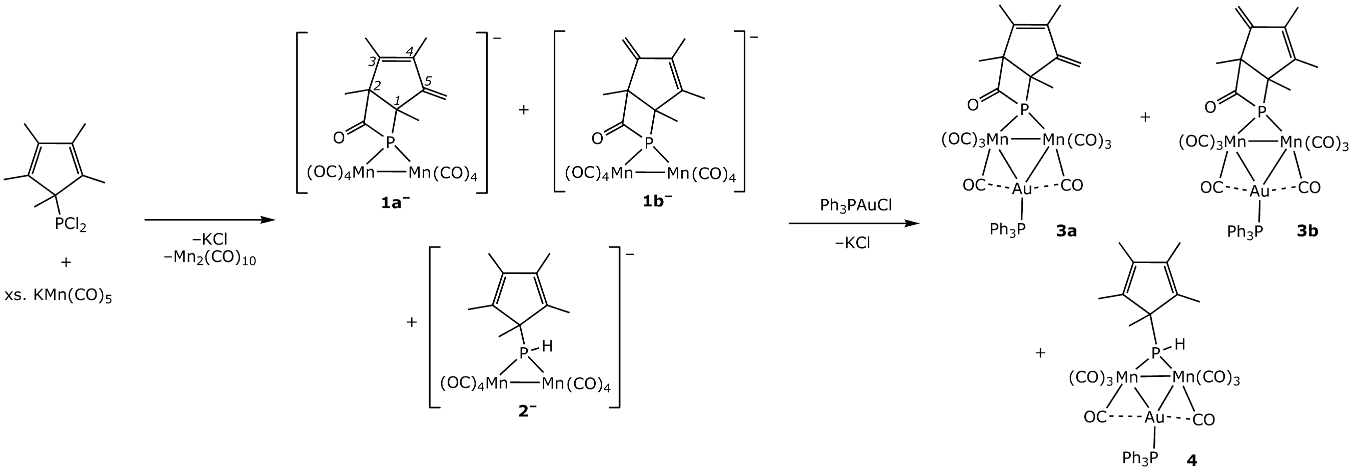
With this versatile and rich chemistry of the tungsten derivative in mind, we tried to extend the general concept of bridging phosphinidene complexes to Mn-substituted derivatives of the type [Cp*P{Mn(CO)$_5$}$_2$], which are unknown up to now. As reactions of dihalogenophosphines with anionic metallates represent the most usual way for the synthesis of such phosphinidene complexes, we have studied the reaction of Cp*PCl$_2$ with KMn(CO)$_5$. Surprisingly, the aforementioned reaction leads to a rapid reduction of the resulting species accompanied by deprotonation and rearrangement reactions and the formation of novel types of bicyclic phosphorus-containing complexes. The results are reported herein.

■ RESULTS AND DISCUSSION

Synthesis. The reaction of Cp*PCl$_2$ with an excess of KMn(CO)$_5$ (Scheme 1) was not accompanied by a drastic color change, and the ^{31}P NMR spectra of the reaction mixture did not contain any signals at low field either. These features usually correspond to the formation of a M−P−M delocalized bond of type **A**−**D** compounds.[20] After the evaporation of the solvents, the only neutral reaction product that could be extracted with hexane was Mn$_2$(CO)$_{10}$ (as shown by IR spectroscopy). The other products seemed to be ionic and were soluble only in polar solvents such as THF and DME. After washing off the formed Mn$_2$(CO)$_{10}$ with hexane, the remaining solid was extracted with ether. Addition of 18-crown-6 and cooling led to the precipitation of red crystals identified as the ionic compound [K(18-crown-6)(Et$_2$O)][Mn$_2$(CO)$_8$(μ-C$_{11}$H$_{14}$OP)] ([K(18-crown-6)(Et$_2$O)][**1**]) by X-ray crystal structure analysis (Figure 1). The structure of the anion shows substantial changes of the former Cp* substituent. Its ring is distorted and one additional CO group bridges the C2 atom of the Cp* ring and the P1 atom. So, a four-membered ring is formed in addition to the initial five-membered one. The P atom binds two Mn(CO)$_4$ fragments that are additionally connected by a Mn−Mn bond.

Only two anionic products were detected by measuring an ESI mass spectrum of the DME solution of the remaining solid after the extraction of Mn$_2$(CO)$_{10}$: the one with the mass of 527.0 corresponds exactly to the anion [**1**]$^-$, while the other one, with a mass of 501.1, has one CO group less than [**1**]$^-$. Low tube lens voltage settings (20 V) were applied to avoid decomposition of the reaction components. The relative intensities (100% and 70%) indicate that both compounds are present in the reaction mixture in comparable amounts. Unfortunately, we did not succeed in crystallizing the second ionic compound separately from the reaction mixture (*vide infra*).

Scheme 1. Synthesis of the Anionic Phosphorus Complexes of Manganese and the Subsequent Transformation into the Neutral Gold Derivatives



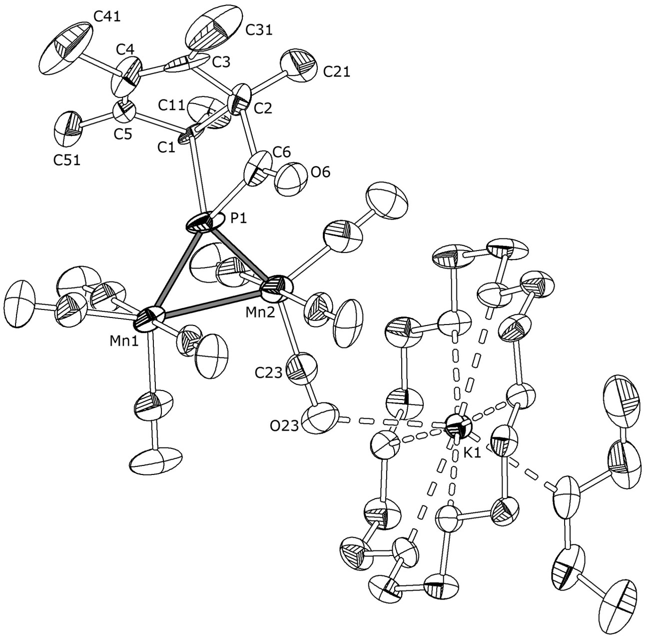


Figure 1. Cation and anion of $[K(18\text{-crown-}6)(Et_2O)][Mn_2(CO)_8(\mu\text{-}C_{11}H_{14}OP)]$ ($[K(18\text{-crown-}6)(Et_2O)][\mathbf{1}]$) (thermal ellipsoids at the 50% probability level, only one part of the disordered bicyclic moiety P1,C1−C6 is shown). Hydrogen atoms are omitted for clarity. Selected bond distances (Å): Mn(1)−P(1) 2.2337(19); Mn(1)−Mn(2) 2.8545(14); Mn(2)−P(1) 2.2606(19); P(1)−C(6) 1.838(12); P(1)−C(1) 1.913(14); C(6)−O(6) 1.221(12); C(6)−C(2) 1.585(18); C(1)−C(2) 1.565(19); C(2)−C(3) 1.595(19); C(3)−C(4) 1.30(2); C(4)−C(5) 1.35(2); C(1)−C(5) 1.509(19); C(1)−C(11) 1.66(2); C(2)−C(21) 1.486(19); C(3)−C(31) 1.46(2); C(4)−C(41) 1.533(18); C(51)−C(5) 1.43(2).

To study the anionic products individually, we converted the ionic part of the reaction mixture into neutral derivatives by treatment with PPh_3AuCl. This reaction proceeded without any noticeable decomposition, and the neutral products could be separated by chromatography on TLC plates (silica). The first bright yellow fraction was obtained apart from the others and could be crystallized from hexane. The subsequent X-ray structure analysis identified the crystals as the complex $[Mn_2(CO)_8(\mu\text{-}PHCp^*)(\mu\text{-}AuPPh_3)]$ (**4**) (Figure 2). Unlike the anion $[\mathbf{1}]^-$, this neutral cluster contains an intact Cp* group σ-bound to the P atom and an $AuPPh_3$ fragment bridging the Mn atoms. The heterocyclic P atom carries an additional proton (cf. Crystal Structure Determination for a more detailed discussion).

The next two fractions were eluted as orange bands so close to each other that they could only be separated (yet not completely) after multiple runs on a TLC plate with hexane as an eluent. The second light orange fraction contained only traces of a product of which no single crystals could be obtained. The third orange fraction included as much compound as the first one and was slightly contaminated by the tail of the previous fraction. We succeeded in getting suitable single crystals for an X-ray structure analysis of this fraction by crystallization from *n*-hexane. The crystals were identified as the neutral cluster $[Mn_2(CO)_8(\mu\text{-}C_{11}H_{14}OP)(AuPPh_3)]$ (**3**) (Figure 3). In the bicyclic section, the structure of this compound is reminiscent of that of the anion $\mathbf{1}^-$. Like in **4**, the fragment $AuPPh_3$ is bridging two Mn atoms, forming a neutral molecule.

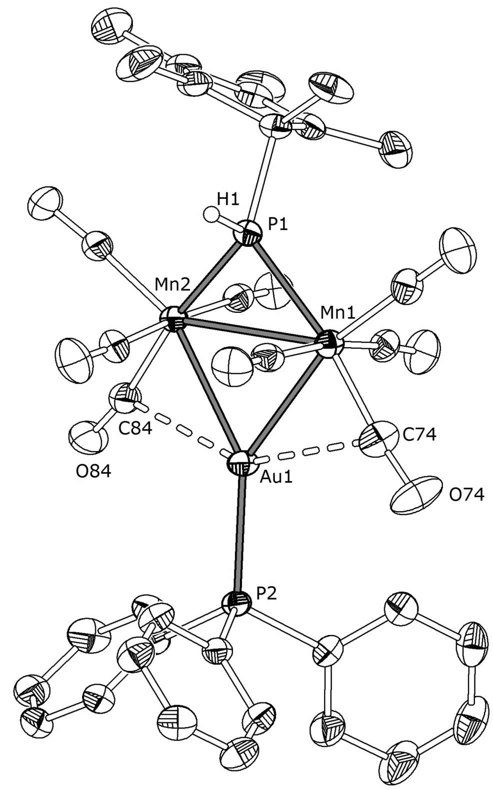


Figure 2. Molecular structure of complex **4** in the crystal (thermal ellipsoids at the 40% probability level). Hydrogen atoms are omitted for clarity. Selected bond distances (Å): Au(1)−P(2) 2.3125(7); Au(1)−C(74) 2.760(4); Au(1)−C(84) 2.673(3); Au(1)−Mn(2) 2.6794(5); Au(1)−Mn(1) 2.6968(4); Mn(1)−P(1) 2.2934(9); Mn(1)−Mn(2) 3.0775(6); Mn(2)−P(1) 2.2682(8); P(1)−H(1) 1.26(3); P(1)−C(1) 1.882(3).

Crystal Structure Determination. Suitable crystals for an X-ray analysis of $[K(18\text{-crown-}6)(Et_2O)][\mathbf{1}]$ were obtained by crystallization of the anionic reaction products after addition of crown ether. The crystal structure (Figure 1) shows the transformation of the Cp* substituent during the formation of the anion $[\mathbf{1}]^-$. Along with the P atom and an additional CO group, it forms a bicyclic ligand with adjacent four- and five-membered rings. The ring system is disordered over two positions, which were refined with equal occupancies. Both rings are almost planar, revealing an angle of 72° between the planes. The distance C6−O6 (~1.22 Å) is typical for a C═O double bond. A more detailed understanding of the geometry and the bonding situation of the ring system could not be deduced solely from the crystallographic data due to a significant overlap of the disordered fragments, which crucially affected the C−C bond distances and did not allow localizing of the hydrogen atoms. The same structure of the anion $\mathbf{1}^-$ of a somewhat poorer quality was obtained for the salt without 18-crown-6, $[K(Et_2O)_2][\mathbf{1}]$ (cf. Supporting Information). After treatment of the mixture of the ionic products with PPh_3AuCl, the crystal structures for both resulting neutral products have fortunately been determined. The molecular structure of **3** (Figure 3) reveals the same bicyclic unit as the anion $[\mathbf{1}]^-$. The four-membered rings in both compounds possess similar geometrical parameters (the maximum differences of the corresponding bond lengths are 0.05 Å). The distances between the remaining three C atoms of the five-membered ring (C3−C5) and from these atoms to their adjacent carbon

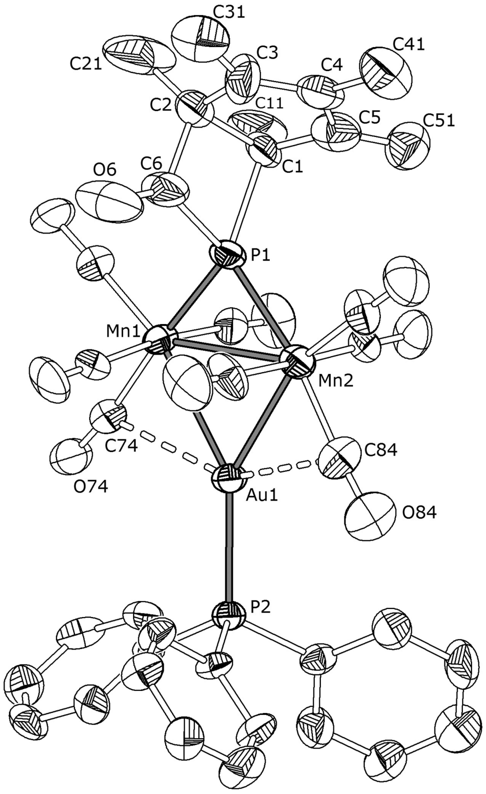


Figure 3. Molecular structure of complex **3** in the crystal (thermal ellipsoids at the 40% probability level). Hydrogen atoms are omitted for clarity. Selected bond distances (Å): Au(1)−P(2) 2.326(4); Au(1)−C(74) 2.718(18); Au(1)−C(84) 2.649(17); Au(1)−Mn(1) 2.669(2); Au(1)−Mn(2) 2.719(2); Mn(1)−P(1) 2.255(5); Mn(1)−Mn(2) 3.081(4); Mn(2)−P(1) 2.259(5); P(1)−C(6) 1.828(18); P(1)−C(1) 1.947(17); C(6)−O(6) 1.23(2); C(1)−C(2) 1.63(2); C(2)−C(3) 1.49(3); C(3)−C(4) 1.33(2); C(4)−C(5) 1.47(2); C(1)−C(5) 1.42(2); C(1)−C(11) 1.54(2); C(2)−C(21) 1.43(3); C(3)−C(31) 1.48(3); C(4)−C(41) 1.52(2); C(5)−C(51) 1.33(2); C(2)−C(6) 1.59(2).

atoms (C31−C51) sufficiently differ in compounds **3**, [K(18-crown-6)(Et_2O)][**1**], and [K(Et_2O)$_2$][**1**], however. These differences may be attributed to the disorder of the bicyclic moiety featuring both ionic structures (cf. Supporting Information). In comparison to the initial Cp* moiety, the C2 atom became quaternized, unlike the atoms C3−C5. According to the X-ray data, the atoms C3, C4, and C5 as well as all the adjacent C atoms lie nearly in one plane. Such a planarity can be explained by a chain of sp^2-hybridized carbon atoms. Hence, supposing the bicyclic moiety is neutral and electron-even, two conjugated double bonds in the chain C31−C3−C4−C5−C51 must be present: either between C3═C31 and C4═C5 or between C3═C4 and C5═C51 (see the NMR Study section for further insight). In the structure of **3**, the bonds C3−C4 and C5−C51 (both 1.33 Å) are significantly shorter than C4−C5, C3−C4, and C4−C41 (1.47−1.52 Å). The thermal ellipsoids of the carbon atoms are not stretched significantly along the bonding direction. Thus, these shorter distances can be considered as double bonds (typical values are 1.33−1.38 Å for double bonds and 1.44−1.52 Å for single bonds for similar conjugated structures with five-membered rings[21]). Therefore, atom C51 represents a CH_2 group and not a CH_3 group like in the initial Cp* fragment. The length of the bond C4−C41 is in the range 1.47−1.59 Å in all structures and can be regarded as a single bond.

In the crystal structure of the second neutral main product, **4** (Figure 2), an intact Cp* moiety is σ-bound at the P atom. The environment of the P atom is not planar (which would be expected for the bridging phosphinidene complexes with a delocalized M−P−M bond), but distorted tetrahedral with three vertices occupied by two Mn and one C atom. The fourth position can be assigned to a H atom, which was found from the difference electron map and refined isotropically without further restraints. The existence of this H atom was further confirmed by NMR and MS data (*vide infra*). Thus, the [Cp*PH] fragment donates three electrons to the two Mn fragments. The counting of one further VE from the $AuPPh_3$ fragment and $8e^-$ from the four CO groups yields $34e^-$ for the dimanganese fragment, which supports the existence of a Mn−Mn single bond according to the 18 VE rule. A related dimanganese complex, [$Mn_2(CO)_8$(μ-PCyH)(μ-$AuPPh_3$)],[22] with a bridging (μ-PHR) phosphido ligand and (μ-$AuPPh_3$) unit reveals very similar structural and spectroscopic properties. The Mn−Mn bond length in **4** (3.076 Å) lies within the normal range of known Mn−Mn distances (2.664−3.244 Å for

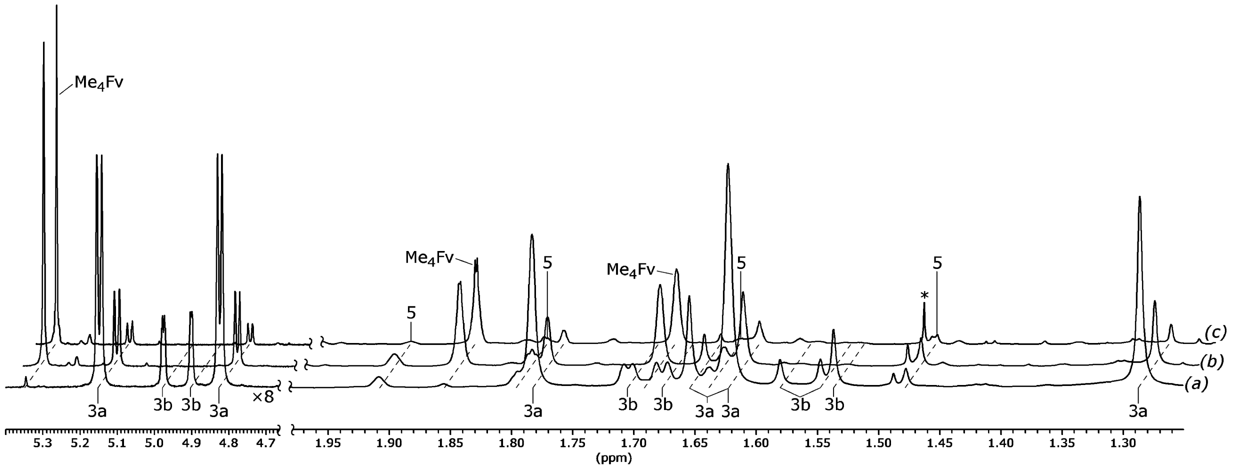


Figure 4. Sections of the ^1H NMR spectra (a) of a mixture of **3a** and **3b** in C_6D_6 and (b, c) after decomposition under diffuse sunlight. The lower field part of the NMR spectrum contains signals of CH_2 groups; the higher field part, those of CH_3 groups. The lower field part is multiplied by 8 for clarity. The asterisk denotes a minor signal of unknown origin.

complexes with a $(CO)_4Mn{-}Mn(CO)_4$ fragment and 3.040−3.136 Å for compounds of the type $Mn_2(CO)_8(\mu\text{-}AuPR_3)(\mu\text{-}PR_2)$ according to the Cambridge Structural Database). The Mn−Mn distance in **3** (3.081 Å) is almost the same as in **4**. In the structure of $[\mathbf{1}]^-$ the Mn−Mn bond is noticeably shorter (2.855 Å), which agrees with the absence of the second bridging group (μ-$AuPPh_3$) and is typical for phosphorus-bridged dimanganese complexes containing a $Mn_2(CO)_8(\mu\text{-}PR_2)$ fragment[21] (2.846−2.951 Å). The cycles P1Mn1Mn2Au1 in the structures of **3** and **4** are nearly planar. Two CO groups in each cluster may be considered as semibridging between the Mn and Au atoms (C74O74 and C84O84), and the angles Mn−C−O lie in the range 170−174°. The C···Au distances vary from 2.649 to 2.760 Å.

NMR Study. The NMR spectroscopic investigations provide further information about the structure of the reaction products. In the ^1H NMR spectrum of **4**, three different sharp resonances for the three CH_3 groups are found that are typical for a σ-bound Cp* moiety.[23] The P−H resonance at 5.20 ppm reveals a doublet ($^1J_{PH}$ = 308 Hz), and the corresponding doublet in the ^{31}P spectrum arises at 181 ppm.

The second fraction of the chromatographic separation containing **3** reveals two similar sets of signals with a ratio of about 4:1 in the ^1H NMR spectra (Figure 4a). Both sets show proton signals around 5 ppm that correspond to CH_2 groups and an additional four signals of four different CH_3 groups with appropriate integral values. The presence of one CH_2 and four CH_3 resonances for each set was also proven by a ^{13}C DEPT experiment that shows all the corresponding resonances as two sets of similar signals. The ^{31}P NMR spectrum reveals two resonances at lower field with the same ratio of intensities at 290 and 277 ppm. Due to this similarity and the fact that the mass spectra illustrate only the presence of two compounds in the mixture of the anionic products, we suppose the presence of two isomers of compound **3** (namely, **3a** and **3b**) in the reaction mixture. They differ in the position of the CH_2 group in the five-membered carbon ring (Figure 5). It was further shown by the X-ray data of **3** (*vide supra*) and $[K(OEt_2)_2][\mathbf{1}]$ (see Supporting Information) that **3a** is the more abundant isomer.

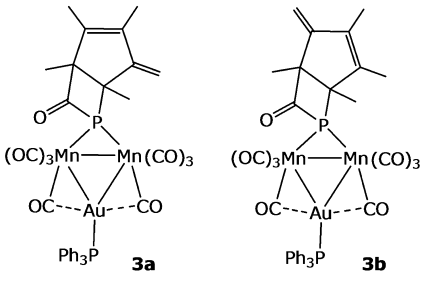
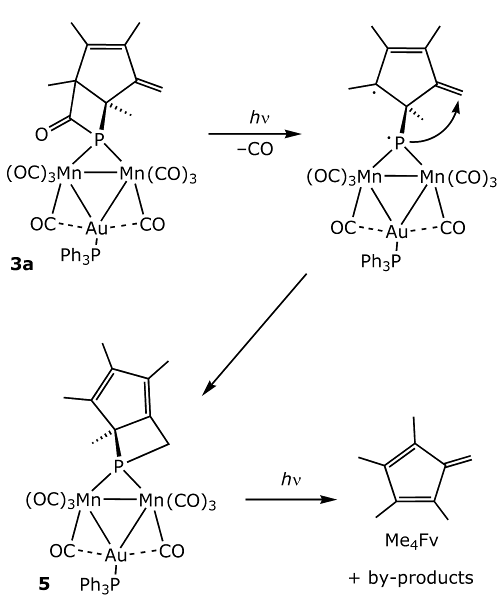


Figure 5. Proposed structures for both isomers of 3.

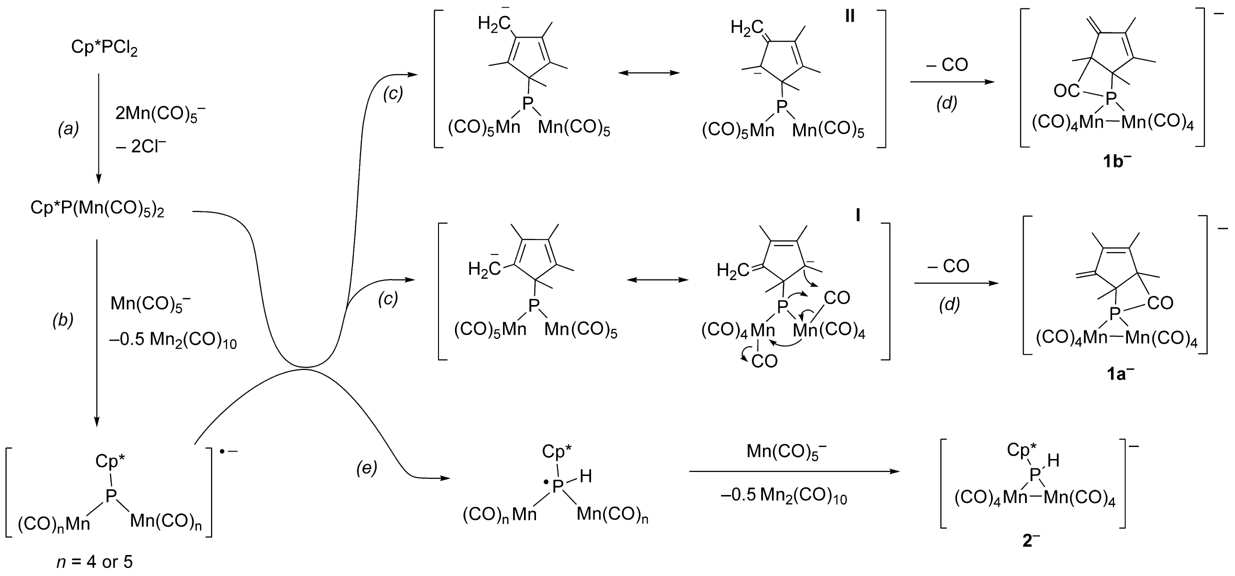
As already mentioned, separation of isomers **3a** and **3b** was not possible by column chromatography, and they were eluted together as an orange band. While trying to separate the isomers by TLC, **3b** disappears according to NMR monitoring. A light-induced decomposition was supposed, which was proven by a separate experiment. After the chromatographic separation, a sealed NMR tube containing a C_6D_6 solution of both isomers was exposed to diffuse sunlight, and ^1H NMR spectra were taken periodically. The intensity of the signals of both **3a** and **3b** subsided gradually. After two days, the signals of **3b** had disappeared (Figure 4b), and the signals of **3a** were reduced by a factor of about seven in four days (Figure 4c). At the same time, three new resonances increased that coincide with those known for tetramethylfulvene (Me_4Fv) (the corresponding signals have also been found in the ^{13}C spectrum).[24] No further signals of noticeable intensity have been monitored in the ^1H NMR spectrum, which indicates that the decomposition of the isomers **3** into Me_4Fv is the main reaction route.

Along with the signals of Me_4Fv, a new set of weaker signals containing one methylene and four methyl resonances appeared in the mixture and decreased after a prolonged irradiation concurrently with those for the isomers of **3**. We were able to separate small amounts of the corresponding compound **5** as a narrow band on a TLC plate. Its ^1H NMR spectrum contains two characteristic CH_2 multiplets noticeably shifted to a higher field in comparison with the signals of **3**. The ^{13}C and ^{31}P NMR spectra of **5** show the same number of resonances as those of **3a** and **3b**, although the signals of the phosphorus atom and the carbon atom of a CH_2 group are shifted to higher field. ^{13}C DEPT measurements confirm that the signal at 28 ppm belongs to a CH_2 group. Nevertheless, this chemical shift and the shifts of the corresponding protons in the ^1H NMR are too much shifted upfield to represent a terminal CH_2 group. This fact, as well as the large H−H coupling constant of 14 Hz, allows the assignment of this resonance to a bridging CH_2 group. In addition, the ^{31}P NMR chemical shift of the P atom (233 ppm) indicates the presence of a μ-PR_2 ligand (cf. 249 ppm for the related complex $[Mn_2(CO)_8(\mu\text{-}PCy_2)(\mu\text{-}AuPPh_3)]$).[25] Hence, one can propose that **5** represents a phosphacyclobutane derivative originated from the elimination of a CO group from the four-membered cycle of **3a**, followed by a radical-induced cyclization with the terminal CH_2 group and a rearrangement of the conjugated double bonds (Scheme 2). The transient compound **5** is then degraded under prolonged irradiation to give Me_4Fv. The stereochemistry of the isomer **3b** does not allow it to be transformed into **5** by an analogous pathway. Still, it is possible that **3b** is decomposed to give Me_4Fv via other transient

Scheme 2. Proposed Reaction Route of the Light-Induced Decomposition of 3



Scheme 3. Proposed Pathway of the Reaction of Cp^*PCl_2 with $KMn(CO)_5$: (a) Substitution of Cl^- by Pentacarbonylmanganate Units; (b) Reduction of the Obtained Complex by a Third Equivalent of $[Mn(CO)_5]^-$; (c) Abstraction of a Proton from the Neutral Complex by the Reduced Complex, Followed by a Mesomeric Stabilization of the Obtained Anion; (d) Intramolecular Nucleophilic Attack of a CO Group, Accompanied by Rearrangement and Formation of a Four-Membered Ring; (e) Binding of a Proton by the Reduced Phosphinidene Complex to Form a Neutral Protonated Complex with a μ-P(H)Cp* Unit



species, which are not monitored by NMR spectroscopy owing to their low concentration or instability. The mentioned photodecomposition is not known for 2-phosphacyclobutanones. To the best of our knowledge, there are only two reports on 2-phosphacyclobutanones as stable compounds to date,[26] and one example represents a ligand of a W complex.[13a] However, the all-carbon analogues, the cyclobutanones, represent a broadly studied class of compounds. Their photochemical decarbonylation leading to the formation of 1,3-biradical was shown to be the predominant pathway for triplet-sensitized reactions.[27−30] The further photodecomposition of **5** can be facilitated by coordination of the P atom to two metal centers, as well as by the release of the stable Me_4Fv in the reaction course. Imine elimination ($Pr^iN{=}CMe_2$) was reported for a μ-PN*i*Pr$_2$ ligand coordinated to two metal centers upon α-C−H activation,[31] which is somewhat comparable to the process found in **5**. For **5**, decomposition products with Mn, Au, and P atoms could not be isolated or identified. The ^{31}P NMR spectrum of the reaction mixture indicates the formation of a large number of unknown P-containing species.

Interestingly, the resonances in the ^{1}H, ^{13}C, and ^{31}P NMR spectra of the reaction mixture of Cp^*PCl_2 with $KMn(CO)_5$ are similar to those of the compounds **4**, **3a**, and **3b** with only slightly different chemical shifts. No other resonances are present in the spectra. Hence, we suppose that the mixture of ionic compounds is consistent with the corresponding anions $[\mathbf{1a}]^-$, $[\mathbf{1b}]^-$, and $[\mathbf{2}]^-$ (Scheme 1) and that the reaction with Ph_3PAuCl results in the formation of the neutral derivatives **3a**, **3b**, and **4**.

The ^{1}H NMR spectrum of the anion $[\mathbf{2}]^-$ features a doublet with a large coupling constant corresponding to the P−H bond (3.49 ppm, J = 317 Hz) for which an analogous doublet arises at 149 ppm in the ^{31}P NMR spectrum. The signals of both isomers of $[\mathbf{1}]^-$ reveal similar chemical shifts, and the same ratios of intensity (approximately 3:1 for **1a**:**1b**) were found for their neutral derivatives. In comparison to the neutral derivatives, all the characteristic signals of the ionic compounds (especially those of the central P atom and the CH_2 group) are shifted to higher field, revealing higher electron density. It is noteworthy that in contrast to the neutral congeners no noticeable decomposition of the ionic salts is observed by irradiation with visible light, which is indicated by the absence of the signals at higher field (for the CH_2 group) or those corresponding to tetramethylfulvene.

Reaction Pathway. On the basis of the X-ray structures of all the main reaction products and the NMR evidence of the isomers $[\mathbf{1a}]^-$ and $[\mathbf{1b}]^-$, the following reaction pathway can be proposed. It should be again mentioned that in the majority of the reactions of $RPHal_2$ with various transition metal-centered anions the main reaction products are phosphinidene complexes of the type **A**−**D**, diphosphenes RP=PR, and their derivatives.[6,9−11,32] Both types of compounds are easily identified by their low-field shifts in the ^{31}P NMR spectra,[33] which were not observed for the discussed reactions. The absence of these phosphinidene complexes as reaction products is rather unusual since such complexes are also formed in similar reactions of the metalate monoanions $Co(CO)_4^-$ and $CpMo(CO)_3^-$ with Ph^*PCl_2, which possesses the more sterically demanding Ph* substituent (Ph* = 2,4,6-tBu$_3$C$_6$H$_2$).[5] Thus, in the present case a fast conversion of an initially generated phosphinidene complex of type **A** might be the reason. Thus, one can propose the formation of the dimanganese complex $[Cp^*P\{Mn(CO)_5\}_2]$ in the early stage of the reaction (Scheme 3a) since a halogen substitution usually proceeds rapidly even at low temperatures.[34] The anionic nature of the characterized products **1** and **2** indicates that not only the substitution but also the reduction of the initially formed neutral complexes occurs (Scheme 3b), which is possibly accompanied by the elimination of CO groups. The only suitable reduction agent in the reaction mixture is $[Mn(CO)_5]^-$. This assumption is supported by the experimental detection of $Mn_2(CO)_{10}$ as a byproduct of the reaction and by the observation that the maximum yields of the anionic products are achieved when the reagents $KMn(CO)_5$ and Cp^*PCl_2 are reacted in the ratio of 3:1 (Scheme 3).

The presence of the anions **2**$^-$ with one additional H atom and **1**$^-$ without a terminal H atom as the major products indicates that a H atom transfer also occurred during the reaction. The four-membered cycle in **1**$^-$ containing an additional CO unit evidently arises from an eliminated CO group of a former $Mn(CO)_5$ unit. In order to form a C−C(O) bond, the CO ligand is presumably attacked by the negatively charged C(2) atom (of the C_5 cycle) that has been formed by a rearrangement after hydrogen atom transfer (Scheme 3c). Reactions including a carbanion attack of the C atom in metal carbonyls are widely known. The opening of the Mn(1)−CO bond and the formation of the P−C(O) bond that closes the PC_3 cycle as well as the formation of the Mn(1)−Mn(2) bond and the loss of a Mn(2)−CO ligand can either be a concerted process or a sequence of subsequent reactions (Scheme 3d). The formation of the two different isomers **1a**$^-$ and **1b**$^-$ is possible if the formation of the corresponding carbanion occurs after abstraction of H^+ from the neutral complex $Cp^*P\{Mn(CO)_5\}_2$. The abstraction of H^+ from a C(3)- or C(4)-bound CH_3 group forms the conjugated anion **I**, which is capable of attacking the CO ligand at the Mn complex fragment (Scheme 3c); the abstraction of H^+ from the CH_3 groups bound at C(2) or C(5) results in the formation of the isomer **II**. An appropriate basic species to abstract the proton is the anionic complex $Cp^*P\{Mn(CO)_n\}_2^-$ (n = 4 or 5), which is formed by the reduction of the initial nucleophilic substitution product by $Mn(CO)_5^-$ (Scheme 3b). After abstraction of a proton, this anion will turn into $Cp^*P(H)\{Mn(CO)_n\}_2$ (Scheme 3e), which is further reduced to form anion **2**$^-$. Any participation of water traces or the solvent as a H atom source can be excluded since the solvents had been thoroughly dried prior to use and experiments using THF-d_8 as solvent did not reveal any deuterated products. Another possible base, such as $Mn(CO)_5^-$, can be excluded since the formed $HMn(CO)_5$ would be rather unreactive under the used conditions. Only traces of such a complex among the neutral reaction products could be detected by ^1H NMR spectroscopy at high field, but the intensity of the appropriate signal is negligible. Moreover, the basicity of P-centered anions must be higher than that of $Mn(CO)_5^-$ (pK_a of the conjugated acid is 15.1 in THF[35]). In all reactions the ratio of **1a**$^-$ to **1b**$^-$ was found to be 2.5:1 (^1H NMR data). This may be explained by the higher stability of **I** with respect to **II** owing to the better delocalization of the negative charge over the conjugated diene system in **I**. In order to prove the participation of a base in the abstraction of a proton from the Cp* substituent and the formation of the anions **1**$^-$, we performed the same reaction in the presence of $NaN(SiMe_3)_2$, which is a strong base (the pK_a of the conjugated acid is 25.8 in THF[36]). Although it is a weak nucleophile, it should not be competitive in substitution reactions. The reagents were used in the ratio $CpPCl_2:KMn(CO)_5:NaN(SiMe_3)_2 = 1:2:1$ to exclude the possibility of the reduction stage *b* (Scheme 3), and the anionic reaction mixture was treated with PPh_3AuCl. The NMR spectra of the reaction products showed approximately the same ratio of the isomers **3a** and **3b** as in the initial reaction, but the concentration of **4** was lowered by a factor of 4. Hence, the presence of an additional base actually facilitates the formation of the carbonic products. A similar carbanion-mediated process is supposed by the reaction of $N(SiMe_3)_2^-$ with Cp^*_2PCl.[37] Here no CO ligands are present, and by converting a Cp*P moiety a PC_2 three-membered ring is formed.

It should be noted that if the reaction proceeds according to Scheme 3 and anions **1**$^-$ and **2**$^-$ are the only products, their amounts have to be equal. In fact, the concentration of the isomers of **1**$^-$ was shown to exceed that of **2**$^-$ by a factor of 1.5 to 3.2 depending on the reaction setup (according to NMR spectra). It can be explained by the competition of another base that is also capable of abstracting a proton from the neutral species $Cp^*P\{Mn(CO)_5\}_2$. Since anionic products containing additional protons are limited to **2**$^-$, some other neutral protonated products must be present in the reaction mixture. After washing the ionic products with hexane, noticeable amounts of only one additional compound containing a Cp^*PH_2 moiety were detected (besides $Mn_2(CO)_{10}$). This compound could be characterized only by NMR spectroscopy. It shows all the signals of a σ-bound Cp* substituent[24] (^1H NMR in C_6D_6 [ppm]: 1.66 d, 6H, 4 Hz, CH_3 at C_2 and C_5; 1.60 s, 6H, CH_3 at C_3 and C_4; 0.95 d, 3H, 14 Hz, C(1)−CH_3) and a doublet at 4.36 ppm with a large coupling constant of 320 Hz in the ^1H NMR spectrum. This corresponds to a PH_2 group since in the ^{31}P NMR spectrum a triplet at 4.9 ppm revealing the same coupling constant is detected. These signals cannot be assigned to free Cp^*PH_2.[24] This compound may arise from a further protonation of the anion **2**$^-$ and may represent a Cp^*PH_2 phosphine coordinated to a Mn carbonyl complex. The ^1H NMR pattern and the coupling constants of this compound are similar to those of $(Cp^*PH_2)Cr(CO)_5$.[38]

An alternative pathway of the reaction can be proposed by a transfer of a H radical from a neutral phosphinidene complex initially formed by its reduced radical anion, followed by a radical attack on the CO carbon atom to form the four-membered cycle. This way is not very likely since the radical attack on a coordinated CO group is an unusual process and shown by calculations to be energetically less favorable.[39] Another quite possible pathway would include fast conversion of the initial phosphinidene complex into a radical anion, which could either react with itself to provide a H radical transfer or gain and release H atoms by separate pathways. To check this possibility, we reacted Cp^*PCl_2 and $KMn(CO)_5$ with $CoCp_2$ as an innocent 1*e* reduction agent (the redox potential of $CoCp_2^{+/0}$, −0.85 V vs SCE,[40] is close to that of $0.5Mn_2(CO)_{10}/Mn(CO)_5^-$, −0.69 V vs SCE[41]) in the molar ratio 1:2:1. The ^1H NMR spectra of the reaction mixture did not contain characteristic signals of complex **2**$^-$, and only traces of **1**$^-$ were detected. Instead, they contained signals of a σ-bound Cp* group and a signal of the $[CoCp_2]^+$ cation, which means the reduction actually took place. Possibly, faster reduction results in a complete conversion of the transient phosphinidene complexes to the radical anion (Scheme 3b), which is incapable of further reaction with itself or acquiring a H atom under the reaction conditions. The presence of radical species is indirectly supported by a noticeable shift of all resonances to higher field, the biggest found for $[CoCp_2]^+$ as a consequence of the interaction. In summary the proposed pathway of proton transfer reactions (Scheme 3) seems to be the most realistic one, although the proceeding of other pathways cannot be completely ruled out.

■ CONCLUSIONS

The reaction of $K[Mn(CO)_5]$ with Cp^*PCl_2 has been shown to be a rare example of an intra- and intermolecular rearrangement reaction involving the reduction of an initially formed phosphinidene species, H atom transfer, and the formation of a new bicyclic ligand by activating the Cp* moiety along with an incorporation of a CO ligand. On the basis of a used excess of the reducing anion $[Mn(CO)_5]^-$ several reactivity centers are necessary for such a complex reaction process such as the presence of a labile CO ligand and a Cp* group that is acidic enough to be diprotonated by a P-centered anion. This combination of reaction centers is unique for the formation of phosphinidene complexes, which usually occurs directly in one step to form conventional complexes of type **A**–**D**. Moreover, to the best of our knowledge, the observed reduction of planar phosphinidene complexes of the type $RP(ML_n)_2$ has not yet been reported. We believe that the reductive activation of phosphinidene complexes might present a useful way for the synthesis of novel P-heterocyclic ligands and metal complexes.

■ EXPERIMENTAL SECTION

All manipulations were performed under argon or nitrogen by using Schlenk techniques or gloveboxes. The starting reagents were prepared according to the known methods: $K[Mn(CO)_5]$[42] and Cp*PCl_2.[24] All solvents were distilled in an inert atmosphere by using common drying agents. TLC plates (Merck silica gel 60) were dried in an oven and transferred into the glovebox.

The NMR spectra were recorded on a Bruker Avance 400 spectrometer (^{1}H: 400.132 MHz, ^{13}C{^{1}H}: 100.632 MHz, ^{31}P: 162.016 MHz) in THF-d_8 or CD_2Cl_2. Chemical shifts (δ, ppm) were referenced to 85% H_3PO_4 (^{31}P) or to the signals of the solvent (^{1}H and ^{13}C, $\delta_H = 3.58$ ppm (THF-d_8), 5.31 ppm (CD_2Cl_2); $\delta_C = 25.2$ ppm (THF-d_8), 54.0 ppm (CD_2Cl_2)). Mass spectra of ionic compounds were measured on a Finnigan ThermoQuest TSQ 7000 spectrometer (ESI, solutions in DME, negative region, tube lens 20 V). IR spectra were recorded in THF solutions. Elemental analysis was carried out on a Eurovector EuroEA3000 CHN analyzer.

Reaction of Cp*PCl$_2$ with KMn(CO)$_5$. Synthesis of [K(OEt$_2$)$_2$]-[1]. A solution of Cp*PCl_2 (0.200 g, 0.844 mmol) in 5 mL of THF was added under stirring to a suspension of $KMn(CO)_5$ (0.600 g, 2.56 mmol) in 10 mL of THF at −60 °C. The initially slightly green solution was stirred at this temperature for one hour. During this time, the color turned to yellow. The stirring was continued overnight at room temperature. The resulting orange, turbid solution was filtered to remove the precipitated (KCl), and the filtrate was evaporated to dryness. The remaining solid was washed with hexane until the washings were no longer colored by $Mn_2(CO)_{10}$ (3 × 30 mL) and then dried in a vacuum. The solid mixture of ionic compounds was used for the NMR (as a solution in THF-d_8) and MS studies as well as for the subsequent reactions. Yields (based on the composition, determined by NMR): **1**$^-$, 46%; **2**$^-$, 31%. The pure crystalline product [K(OEt$_2$)$_2$][**1**] (mixture of isomers) was obtained by the extraction of the product mixture with ether followed by crystallization at −30 °C. The crystalline product [K(18-crown-6)(Et$_2$O)][**1**] was obtained in a mixture with salts of **2**$^-$ after the addition of an approximately equimolar amount (with respect to the starting phosphine) of dry 18-crown-6 ether to the ether extract followed by cooling at 4 °C overnight. Single crystals suitable for X-ray diffraction were taken from the group of formed crystals. ESI-MS of the solid mixture of products: 527.0 (**1**$^-$), 501.1 (**2**$^-$).

Compounds [K(OEt$_2$)$_2$][**1**] and [K(18-crown-6)(Et$_2$O)][**1**] (atom numbering is consistent with that shown for crystal structures) (mixture of the isomers *a* and *b*, only signals of the anionic part are given, THF-d_8): ^{1}H NMR: 4.98 (d, $^4J_{PH} = 6$ Hz), 4.66 (d, $^4J_{PH} = 6$ Hz; the last two signals correspond to the $CH_2{}^a$ group), 4.72 (dd, $^5J_{PH} = 2$ Hz, $^2J_{HH} = 0.6$ Hz), 4.58 (dd, $^5J_{PH} = 3$ Hz, $^2J_{HH} = 0.6$ Hz; the last two signals correspond to the $CH_2{}^b$ group), 1.87 (m), 1.73 (m), 1.42 (s; the last three signals correspond to the C(2)−$CH_3{}^b$, C(4)−$CH_3{}^b$, and C(5)−$CH_3{}^b$ groups), 1.80 (m), 1.75 (m), 1.19 (s; the last three signals correspond to the C(2)−$CH_3{}^a$, C(3)−$CH_3{}^a$, and C(4)−$CH_3{}^a$ groups), 1.48 (d, C(1)−$CH_3{}^a$, $^3J_{PH} = 15$ Hz), 1.44 (d, C(1)−$CH_3{}^b$, $^3J_{PH} = 15$ Hz). ^{13}C{^{1}H} NMR: 239, 227 (both br s, Mn−CO), 237.8 (d, C=O^b, $^1J_{PC} = 7$ Hz), 236.1 (d, C=O^a, $^1J_{PC} = 11$ Hz), 162.9 (d, $J_{PC} = 1$ Hz), 140.5 (s), 135.7 (d, $J_{PC} = 2$ Hz; the last three signals correspond to the atoms C(2)^a, C(3)^a, and C(4)^a), 156.9 (s), 150.6 (d, $J_{PC} = 2$ Hz), 132.9 (d, $J_{PC} = 8$ Hz; the last three signals correspond to the atoms C(2)^b, C(4)^b, and C(5)^b), 102.8 (d, $CH_2{}^a$, $^3J_{PC} = 9$ Hz), 99.1 (d, $CH_2{}^b$, $^5J_{PC} = 6$ Hz), 87.6 (d, C(1)^a, $^1J_{PC} = 33$ Hz), 82.4 (d, C(1)^b, $^1J_{PC} = 33$ Hz), 56.6 (d, C(3)^b, $^2J_{PC} = 20$ Hz), 49.0 (d, C(5)^a, $^2J_{PC} = 19$ Hz), 20.9 (d, C(1)−$CH_3{}^a$, $^2J_{PC} = 7$ Hz), 19.0 (d, C(1)−$CH_3{}^b$, $^2J_{PC} = 9$ Hz), 17.5 (d, $J = 1$ Hz), 12.3 (d, $J = 2$ Hz), 10.4 (d, $J = 2$ Hz; the last three signals correspond to the atoms C(2)−$CH_3{}^b$, C(4)−$CH_3{}^b$, and C(5)−$CH_3{}^b$), 14.0 (d, $J = 4$ Hz), 11.3 (s), 10.5 (s; the last three signals correspond to the atoms C(2)−$CH_3{}^a$, C(3)−$CH_3{}^a$, and C(4)−$CH_3{}^a$). The CH_2 groups are confirmed by a DEPT 135 experiment. ^{31}P NMR: 260^a (s, br), 243^b (s, br). IR (ν_{CO}): 1711 (m), 1899 (s), 1922 (m), 1939 (s), 1946 (w,sh), 1968 (w,sh), 1978 (s), 2039 (s) cm^{-1}.

Anion **2**$^-$ (based on the subtraction of the signals of **1a**$^-$ and **1b**$^-$ from the spectrum of the mixture of compounds): ^{1}H NMR: 3.49 (d, 1H, PH, $^1J_{PH} = 317$ Hz), 2.00 (s, 6H, C(2)−CH_3 and C(5)−CH_3), 1.75 (d, 6H, C(3)−CH_3 and C(4)−CH_3, $^5J_{PH} = 2$ Hz), 0.97 (d, 3H, C(1)−CH_3, $^3J_{PH} = 18$ Hz). ^{13}C{^{1}H} NMR: 143.4 (d, C(3) and C(4), $^3J_{PC} = 3$ Hz), 133.6 (d, C(2) and C(5), $^2J_{PC} = 5$ Hz), 60.1 (s, C(1)), 17.6 (d, C(1)−CH_3, $^2J_{PC} = 7$ Hz), 11.8 (d, C(2)−CH_3 and C(5)−CH_3, $^3J_{PC} = 3$ Hz), 11.3 (s, C(3)−CH_3 and C(4)−CH_3). ^{31}P NMR: 149 (d, $^1J_{PH} = 320$ Hz).

Syntheses of 3, 4, and 5. At −78 °C, a solution of PPh_3AuCl (0.40 g, 0.81 mmol) in 10 mL of THF was added dropwise to a solution of the mixture of the anionic salts from the above-described reaction (0.40 g, ca. 0.71 mmol **1**$^-$ + **2**$^-$) in 10 mL of THF. After half an hour the mixture was allowed to warm to room temperature, filtered, and evaporated to a volume of ca. 2 mL. According to NMR spectroscopy, the reaction proceeds nearly quantitatively. Half of the mixture was separated by column chromatography (silica gel, hexane−toluene mixtures), and compound **4** (first band, bright yellow) and a mixture of **3a** and **3b** (second band, orange) were obtained. The other half of the product mixture was separated by TLC (silica plates, hexane), and compounds **4** (first band), **5** (second weak band, yellow-orange), and **3a** (third band) were isolated. Two weak bands, which came in front of the second and after the third ones, contained very small amounts of products, which could not be characterized. The plates were cut and extracted with THF. The solutions were dried under vacuum, and all the compounds were recrystallized separately from hexane. Isolated yields (based on the amount of starting material): 90 mg (27%) for **4** and 62 mg (18%) for **3a**. Compound **5** was characterized only by NMR due to the small amounts formed.

Compound **3a**: ^{1}H NMR (CD_2Cl_2): 7.62−7.42 (m, 15H, Ph), 5.15 (d, 1H, CH_2, $^2J_{HH} = 7$ Hz), 4.69 (d, 1H, CH_2, $^2J_{HH} = 6$ Hz), 1.88 (s, 3H), 1.84 (s, 3H), 1.43 (s, 3H, the last three signals correspond to the C(2)−CH_3, C(3)−CH_3, and C(4)−CH_3 groups), 1.62 (d, 3H, C(1)−CH_3, $^3J_{PH} = 16$ Hz). ^{13}C{^{1}H} NMR: 225.3 (d, C=O, $^1J_{PC} = 10$ Hz), 162.3 (d, $J_{PC} = 2$ Hz), 139.5 (s), 137.0 (d, $J_{PC} = 2$ Hz; the last three signals correspond to the atoms C(2), C(3), and C(4)), 134.6 (d, 6C, *o*-Ph, $^2J_{PC} = 14$ Hz), 132.4 (d, *i*-Ph, $^1J_{PC} = 45$ Hz), 131.7 (d, 3C, *p*-Ph, $^4J_{PC} = 2$ Hz), 129.7 (d, 6C, *m*-Ph, $^3J_{PC} = 11$ Hz), 104.6 (d, 1C, CH_2, $^3J_{PC} = 9$ Hz), 90.3 (d, C(1), $^1J_{PC} = 37$ Hz), 51.1 (d, C(5), $^2J_{PC} = 21$ Hz), 20.6 (d, 1C, C(1)−CH_3, $^2J_{PC} = 5$ Hz), 13.5 (d, 1C, $^3J_{PC} = 5$ Hz), 11.8 and 10.8 (both s, 1C, the last three signals correspond to the atoms C(2)−CH_3, C(3)−CH_3, and C(4)−CH_3). The CH_2 group is confirmed by a DEPT 135 experiment. ^{31}P NMR: 290 (s, 1P, PMn_2), 65 (s, 1P, PPh_3). IR (ν_{CO}): 1701 (m), 1912 (s), 1942 (s), 1960 (m), 2007 (s), 2050 (s) cm^{-1}.

Compound **3b** (based on the subtraction of the signals of **3a** from the spectra of the mixture of isomers): ^{1}H NMR (CD_2Cl_2): 7.62−7.42 (m, 15H, Ph), 5.00 (br s, 1H, CH_2), 4.89 (br s, 1H, CH_2), 1.82 (br s, 3H), 1.58 (s, 3H; the last two signals correspond to two of the three Me groups C(2)−CH_3, C(4)−CH_3, and C(5)−CH_3), 1.70 (d, 3H, C(1)−CH_3, $^3J_{PH} = 17$ Hz). ^{13}C{^{1}H} NMR: 155.5 (s), 147.7 (s), 135.6 (d, $J_{PC} = 8$ Hz; the last three signals correspond to the atoms C(2), C(4), and C(5)), 134.8 (d, 6C, *o*-Ph, $^{2}J_{PC}$ = 14 Hz), 132.2 (d, *i*-Ph, $^{1}J_{PC}$ = 45 Hz), 132.0 (br s, 3C, *p*-Ph), 129.8 (d, 6C, *m*-Ph, $^{3}J_{PC}$ = 12 Hz), 102.4 (d, 1C, CH_2, $^{4}J_{PC}$ = 6 Hz), 84.5 (d, C(1), $^{1}J_{PC}$ = 38 Hz), 59.4 (d, C(3), $^{3}J_{PC}$ = 21 Hz), 18.5 (d, 1C, C(1)−CH_3, $^{2}J_{PC}$ = 6 Hz), 16.9, 13.0, 10.7 (all s, 1C, the last three signals correspond to the atoms C(2)−CH_3, C(4)−CH_3, and C(5)−CH_3). The CH_2 group is confirmed by a DEPT 135 experiment. ^{31}P NMR: 277 (s, 1P, PMn_2), 65 (s, 1P, PPh_3).

Compound **4**: ^{1}H NMR (CD_2Cl_2): 7.59−7.40 (m, 15H, Ph), 5.20 (d, 1H, PH, $^{1}J_{PH}$ = 308 Hz), 1.94 (s, 6H, C(2)−CH_3 and C(5)−CH_3), 1.75 (d, 6H, C(3)−CH_3 and C(4)−CH_3, $^{5}J_{PH}$ = 4 Hz), 1,68 (d, 3H, C(1)−CH_3, $^{3}J_{PH}$ = 17 Hz). ^{13}C{^{1}H} NMR: 139.8 (s, C(3) and C(4)), 138.7 (d, C(2) and C(5), $^{2}J_{PC}$ = 6 Hz), 134.7 (d, 6C, *o*-Ph, $^{2}J_{PC}$ = 15 Hz), 132.6 (d, *i*-Ph, $^{1}J_{PC}$ = 45 Hz), 131.6 (d, 3C, *p*-Ph, $^{4}J_{PC}$ = 2 Hz), 129.6 (d, 6C, *m*-Ph, $^{3}J_{PC}$ = 11 Hz), 60.1 (d, C(1), $^{1}J_{PC}$ = 6 Hz), 21.9 (d, 1C, C(1)−CH_3, $^{2}J_{PC}$ = 3 Hz), 12.0 (d, 2C, C(2)−CH_3 and C(5)−CH_3, $^{4}J_{PC}$ = 2 Hz), 11.6 (d, 2C, C(3)−CH_3 and C(4)−CH_3, $^{5}J_{PC}$ = 2 Hz). ^{31}P NMR: 181 (d, 1P, PH, $^{1}J_{PH}$ = 310 Hz), 63 (s, 1P, PPh_3). Anal. Calcd for $C_{36}H_{31}AuMn_2O_8P_2$: C, 45.02; H, 3.25. Found: C, 44.62; H, 3.40. IR (ν_{CO}): 1932 (s), 1954 (s), 1980 (s), 2018 (s), 2061 (m) cm^{-1}.

Compound **5**: ^{1}H NMR: 7.60−7.42 (m, 15H, Ph), 3.81 (dd, 1H, CH_2, $^{2}J_{HH}$ = 14 Hz, $^{2}J_{PH}$ = 7 Hz), 3.16 (dd, 1H, CH_2, $^{2}J_{HH}$ = 14 Hz, $^{2}J_{PH}$ = 3 Hz), 1.94 (br s, 3H), 1.91 (m, 3H), 1.80 (br s, 3H), 1.55 (s, 3H, all four signals correspond to CH_3 groups). ^{13}C{^{1}H} NMR: 134.6 (d, 6C, *o*-Ph, $^{2}J_{PC}$ = 15 Hz), 132.4 (d, *i*-Ph, $^{1}J_{PC}$ = 45 Hz), 131.7 (d, 3C, *p*-Ph, $^{4}J_{PC}$ = 2 Hz), 129.6 (d, 6C, *m*-Ph, $^{3}J_{PC}$ = 11 Hz), 28.0 (d, 1C, CH_2, $^{1}J_{PC}$ = 13 Hz), 18.7 (s, 1C), 12.0 (s, 1C), 11.2 (br s, 2C, the last three signals correspond to all the CH_3 groups). The CH_2 group is confirmed by a DEPT 135 experiment. ^{31}P NMR: 233 (s, 1P, PMn_2), 65 (s, 1P, PPh_3).

Light Irradiation of the Mixture of the Isomers 3a and 3b. The mixture of the isomers **3a** and **3b** (obtained after chromatographic separation) was dissolved in C_6D_6 and sealed in a NMR tube, which was exposed to diffused sunlight. ^{1}H NMR spectra were periodically monitored. The isomer **3b** fully disappeared after two days, while the concentration of the predominant isomer **3a** decreased by a factor of 2.5 (the residual proton signals of C_6D_6 were used as reference). Simultaneously with the decomposition of **3a** and **3b**, the formation of tetramethylfulvene was noticed, which was identified on the basis of the known ^{1}H and ^{13}C spectra.[24] The remaining **3a** had decomposed almost completely after further three days, but no other signals in the region of CH_3 and CH_2 groups were monitored in the mixture. The ^{31}P NMR spectra showed an increasing number of resonances of low intensity during the decomposition (without a predominant one), which could not be assigned to any known compound.

Reaction in the Presence of $CoCp_2$ As a Reduction Agent. A solution of $KMn(CO)_5$ (0.0391 g, 0.167 mmol) in 0.7 mL of THF-d_8 was slowly added to a cooled (−70 °C) stirred solution of Cp^*PCl_2 (0.0198 g, 0.0835 mmol) in 0.7 mL of the same solvent. After 15 min, a solution of $CoCp_2$ (0.0158 g, 0.0836 mmol) in 0.7 mL of THF-d_8 was added. The mixture was stirred at 30 min at −70 °C and another 2 h at room temperature. The solution was filtered and sealed into a NMR tube. ^{1}H NMR: 4.62 (br s, 10H, Cp), 2.05 (s, 2H, CH_3), 1.81 (s, 2H, CH_3), 1.55 (d, 1H, C(1)−CH_3, $^{3}J_{PH}$ = 14 Hz). ^{2}H NMR: no signals exceeding the noise level except those of the solvent.

X-ray Structure Determination of the Compounds [K(18-crown-6)(Et$_2$O)][1], 3a, and 4. Crystals of [K(18-crown-6)(Et_2O)][**1**] were obtained from a cooled ether solution (−28 °C), while **3a** and **4** crystallized from cooled hexane solutions. Crystal data and experimental details are given in Table S1 (see Supporting Information). X-ray data were collected on a Stoe IPDS diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Corrections for Lorentz and polarization effects, crystal decay, and absorption were applied. The structures were solved by direct methods using the program SHELXS-97.[43a] The structure full-matrix-least-squares refinement on F^2 was carried out with the program SHELXL-97[43b] with anisotropic displacement for non-hydrogen atoms. Hydrogen atoms in **3a** and **4** (except for PH group in **4**) were placed in idealized positions and refined isotropically according to the riding model. In [K(18-crown-6)(Et_2O)][**1**] the P-CO-$C_5Me_4CH_2$ fragment is disordered over two positions with equal weights and significant overlap. Therefore H atom positions in this fragment were not localized. The other H atoms were placed in the geometrical positions. Full details of X-ray structural determinations can be found in the Supporting Information and in CIF files that were deposited in the Cambridge Crystallographic Data Centre under the deposition codes.

■ ASSOCIATED CONTENT

Supporting Information

Details giving experimental and crystal data for [K(18-crown-6)(Et_2O)][**1**], [K(OEt_2)$_2$][**1**], **3a**, and **4** and figures giving the NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC Nos. 901837 ([K(OEt_2)$_2$][**1**]), 919318 ([K(18-crown-6)-(Et_2O)][**1**]), 901838 (**3a**), and 901839 (**4**) contain 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.

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Notes

The authors declare no competing financial interest.

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