tuted η^3-allyl complexes [Mo{*endo-syn*-η^3-1-C_3H_4CHO}$(CO)_2(\eta^5\text{-}C_5Me_5)$] (1)[9] and [Mo{*exo-syn*-η^3-1-C_3H_4CHO}$(CO)_2(\eta^5\text{-}C_5Me_5)$] (2), the minor product (4%) being [Mo{*exo-anti*-η^3-1-C_3H_4CHO}$(CO)_2(\eta^5\text{-}C_5Me_5)$] (3) (see Scheme I).

To gain insight into the chemistry of these functionalized η^3-allyls, their reactivity toward strong acids was examined. The low-temperature (−78 °C, CF_3SO_3H, CH_2Cl_2) protonation of the mixture of **1** and **2**, or the single isomer **3**, afforded respectively on room temperature workup either a mixture (7:3) of the exo and endo isomers of the *trans*-1-hydroxybuta-1,3-diene cationic complexes **5** and **6** or just **5**, in each case with a cisoid geometry about the C_2–C_3 axis (Scheme I). These, unlike the corresponding η^5-C_5H_5 and η^5-C_9H_7 complexes, are not interconvertible and do not isomerize into the η^4-*s-cis,cis*-1-hydroxybuta-1,3-diene cations. Addition of triethylamine to the mixture of **5** and **6** resulted in deprotonation, regenerating **1**, **2**, and **3**, but with **3**, i.e. the exo-anti isomer, now predominating. When **1** and **2** were protonated and then deprotonated at low temperature, only **1** and **2** were regenerated in the original ratio of 7:3 (Scheme I).

The conversion of **5** into **3** can be seen to proceed without alteration to the overall stereochemistry of the carbon skeleton of the coordinated ligand. This was found to be equally applicable to the reverse reaction, thus establishing the nature of the interconversions as being exclusively *anti*-η^3-allyl aldehyde $\rightleftharpoons$ η^4-*s-cis*-1,3-hydroxydiene and suggesting that a similar retention of stereochemistry occurs on protonation of the *syn*-η^3-allyl aldehydes leading to the formation of cationic η^4-*s-trans*-1,3-diene species, which on warmup isomerize to the isolated η^4-*s-cis*-1,3-diene cations. In order to explore this interesting idea, the mixture of **1** and **2** was protonated at low temperature (CF_3SO_3H, CD_2Cl_2, −78 °C) in an NMR tube, resulting in a quantitative conversion into two new cationic species. These were identified unambiguously by ^1H NMR spectroscopy[8] as the η^4-*s-trans*-1-hydroxybuta-1,3-diene complexes **7** and **8** (Scheme I), thereby confirming the predicted *syn*-allyl $\rightleftharpoons$ transoid 1,3-diene relationship. Complexes **7** and **8** were shown to be stable in solution below ca. −40 °C, isomerizing irreversibly at more elevated temperatures into the corresponding cisoid species **6** and **5**, respectively. A comparison between the ^1H NMR spectroscopic data reveals the following points of note. A decrease in the magnitude of $^3J(HH)$ across the C_2–C_3 bond is observed [**7**, 7.7 Hz; **8**, 7.4 Hz; **5**, 6.3 Hz; **6**, 6.3 Hz] upon isomerization (transoid to cisoid) as might be expected.[2,3] Secondly there is a marked upfield shift of the "inside" protons (H^a and H^e) in the cisoid complexes, relative to the values obtained from the elongated transoid analogues.

These novel aldehyde substituted η^3-allyls are also potential precursors of pentadienyl complexes, a class of compounds which are currently attracting attention.[10] Reaction (thf, −78 °C) of **1** and **2** with the Wittig reagent Ph_3PCH_2 afforded a mixture of the *exo*- and *endo-syn*-η^3-pentadienyl complexes **9** and **10** in a ratio of 7:3, i.e. opposite to the exo/endo ratio of the precursor aldehyde-substituted species. A similar reaction between the exo-anti complex **3** and Ph_3PCH_2 afforded only the *exo-anti*-η^3-pentadienyl complex **11**. Thus, these observations establish a new and possibly general synthetic approach to η^3-pentadienyl complexes.

It was of obvious importance to examine the protonation of these η^3-pentadienyl-substituted species. Protonation (−78 °C, CF_3SO_3H, CH_2Cl_2) of the mixture of **9** and **10** followed by room-temperature workup afforded a mixture (7:3) of **16** and **15**, respectively, there being no evidence for the formation of the corresponding η^4-*s-cis,cis*-penta-1,3-diene cations. Similarly, protonation of **11** gave only **15** (Scheme II). Importantly, upon repetition of the protonation reaction in CD_2Cl_2 solution, with the progress of the reaction being monitored by ^1H NMR, it was clear that at low temperature the mixture of **9** and **10** gave only the cations **13** and **14** (*exo*-η^4-*s-trans,trans*-penta-1,3-diene and *endo*-η^4-*s-trans,trans*-penta-1,3-diene substituted species) and that only on warming to −40 °C did these undergo irreversible thermal isomerization to the thermodynamically more stable η^4-*s-cis,trans*-penta-1,3-diene cations **15** and **16**.

Thus in conclusion, these observations show that η^4-*s-trans*-1,3-dienes can in fact be stabilized by the cationic metal fragment $Mo(CO)_2(\eta^5\text{-}C_5Me_5)$. The establishment of regioselectivity for the low-temperature reactions of these η^4-*s-trans*-penta-1,3-diene cations with nucleophilic reagents will be of particular interest.

Acknowledgment. We thank the SERC for support and Professor P. Legzdins for providing valuable comparative NMR data.

Registry No. **1**, 121987-64-2; **2**, 122087-46-1; **3**, 122087-47-2; **5**, 121987-66-4; **6**, 122087-49-4; **7**, 122087-51-8; **8**, 122087-53-0; **9**, 121987-67-5; **10**, 122087-54-1; **11**, 122087-55-2; **13**, 121987-69-7; **14**, 122087-57-4; **15**, 122087-59-6; **16**, 122087-61-0; [Mo$(NCMe)_2(CO)_2(\eta^5\text{-}C_5Me_5)$][$BF_4$], 121987-71-1; Ph_3PCH_2, 3487-44-3; *trans/cis*-1-((trimethylsilyl)oxy)buta-1,3-diene, 6651-43-0.

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[9] A single-crystal X-ray diffraction study (Bates, P.; Green, M.; Hursthouse, M.; Waring, T., unpublished observations) with the related complex [Ru{*exo-syn*-η^3-1-C_3H_4CO}(CO)$(\eta^5\text{-}C_5H_6)$] shows that the carbonyl group of the aldehyde functionality is oriented in the same way as is illustrated in Scheme I for complex **2** and that possibly related to this, there was evidence for π-electron delocalization.

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P–C Bond Activation of Triphenylphosphine. Formation of a Dinuclear μ-η^2:η^2-Benzene Complex of Ruthenium

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Summary: The dinuclear tetrahydride $(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}H)_4Ru(\eta^5\text{-}C_5Me_5)$ reacts with triphenylphosphine to give $(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}PPh_2)(\mu\text{-}H)(\mu\text{-}\eta^2{:}\eta^2\text{-}C_6H_6)Ru(\eta^5\text{-}C_5Me_5)$. The structure of the complex has been determined by a single-crystal X-ray diffraction study, which shows the complex to have an η^4-benzene as a bridging ligand.

In the preceding communication, we reported the synthesis of a novel tetrahydride-bridged dinuclear ruthenium complex, $(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}H)_4(\eta^5\text{-}C_5Me_5)$ (1),[1] and the ac-

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[1] Suzuki, H.; Omori, H.; Lee, D. H.; Yoshida, Y.; Moro-oka, Y. *Organometallics* **1988**, *7*, 2243.

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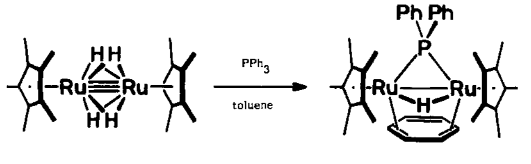
tivation of a C–H bond of ethylene induced by complex 1.[2] During the course of investigating the reactivity of a coordinatively unsaturated species caused by tetrahydride 1 under thermal conditions, the formation of a stable dinuclear μ-η^2:η^2-benzene complex via P–C bond activation of triphenylphosphine was discovered. The η^2- and η^4-arene complexes have received attention in recent years because of their role as intermediates in C–H activation[3] and hydrogenation[4] of arenes. We report herein the preparation, structure determination, and ligand exchange reaction of a novel dinuclear μ-η^2:η^2-benzene complex of ruthenium.

Treatment of (η^5-C_5Me_5)Ru(μ-H)$_4$Ru(η^5-C_5Me_5) (1) with 1.2 equiv of PPh_3 in toluene at room temperature resulted in the formation of (η^5-C_5Me_5)Ru(μ-PPh_2)(μ-H)(μ-η^2:η^2-C_6H_6)Ru(η^5-C_5Me_5) (2) (eq 1). Recrystallization from pentane afforded analytically pure 2 as deep red prisms in a 39% yield based on tetrahydride 1.



(1)

The complex has been characterized by ^1H, ^{13}C, and ^{31}P NMR and infrared spectroscopy and elemental analysis.[5] Notable features of the ^1H NMR spectrum measured in C_6D_6 at room temperature are the resonance signals for the μ-benzene ligand at δ 2.71 (m, 2 H), 2.77 (m, 2 H), and 5.41 (m, 2 H). An upfield shift of the two sets of signals for aromatic protons confirms the coordination of benzene in the μ-η^2:η^2-mode. The spectrum was invariant over the 25–80 °C range. This indicates that the μ-η^2:η^2-benzene ligand is nonfluxional at least over this temperature range.

The resonance for the bridging hydride appeared at δ −16.6 as a doublet due to the spin coupling with the phosphorus nucleus in the μ-phosphido ligand. The $^2J_{PH}$ value of 40.6 Hz for 2 is larger than that for ruthenium-hydride complexes with both C_5Me_5 and tertiary phosphine ligands such as (η^5-C_5Me_5)$RuH_3(PR_3)$ (20–22.5 Hz),[6] (η^5-C_5Me_5)RuH(CO)(PR_3) (34–36 Hz),[7] and (η^5-C_5Me_5)RuH(PMe_3)$_2$ (38 Hz).[8]

In the ^{13}C NMR spectrum, three nonequivalent peaks assignable to the carbons of the coordinated benzene were observed at δ 46.4, 47.8, and 124.3. These values are comparable with those reported for $[(Os(NH_3)_5)_2(\mu$-η^2:η^2-$C_6H_6)]^{4+}$ (49.6, 53.1, and 127.6 ppm)[9] and [(η^5-C_5Me_5)Re(CO)$_2$]$_2$(μ-η^2:η^2-C_6H_6) (40.9, 50.6, and 127.3 ppm).[10]

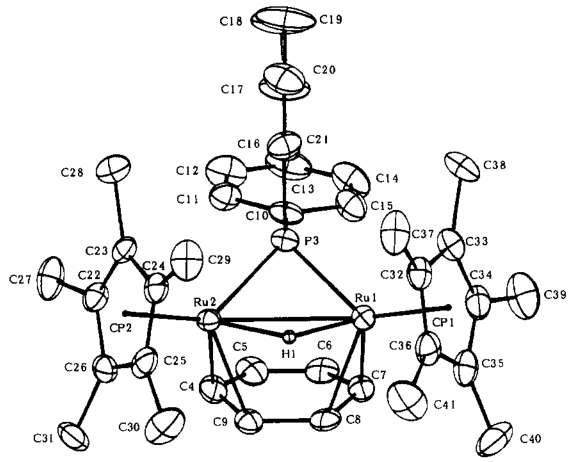


Figure 1. Molecular structure of (η^5-C_5Me_5)Ru(μ-PPh_2)(μ-H)(μ-η^2:η^2-C_6H_6)Ru(η^5-C_5Me_5) (2). Bond lengths (Å) and angles (deg) of interest are as follows: Ru(1)–Ru(2), 2.945 (1); Ru(1)–H(1), 1.56 (9); Ru(2)–H(1), 1.66 (9); Ru(1)–P(3), 2.307 (2); Ru(2)–P(3), 2.308 (2); Ru(1)–C(7), 2.254 (9); Ru(1)–C(8), 2.168 (10); Ru(2)–C(4), 2.248 (10); Ru(2)–C(9), 2.168 (10); Ru(1)–CP(1), 1.883 (1); Ru(2)–CP(2), 1.885 (1); P(3)–C(10), 1.852 (9); P(3)–C(16), 1.834 (8); C(4)–C(5), 1.451 (16); C(5)–C(6), 1.332 (17); C(6)–C(7), 1.441 (15); C(7)–C(8), 1.428 (15); C(8)–C(9), 1.460 (15); C(9)–C(4), 1.442 (16); Ru(1)–H(1)–Ru(2), 133 (6); Ru(1)–P(3)–Ru(2), 79.3 (1); C(10)–P(3)–C(16), 76.6 (4); Ru(1)–C(7)–C(8), 67.9 (5); Ru(1)–C(8)–C(7), 74.4 (6); Ru(2)–C(4)–C(9), 67.9 (5); Ru(2)–C(9)–C(4), 74.0 (6). CP indicates the centroid of a C_5Me_5 ring.

The $^{31}P\{^1H\}$ NMR spectrum of 2 in C_6D_6 revealed a resonance at δ 168.0 assigned to the μ-PPh_2 ligand.[11] It is well established that the ^{31}P resonances appear downfield when μ-PPh_2 ligands bridged two metals joined by a metal–metal bond.[12] The downfield position of the resonance for the phosphido ligand, therefore, implies the presence of a Ru–Ru bond in 2.

A single-crystal X-ray diffraction study of 2 confirmed the proposed structure (Figure 1).[13] The Ru–Ru distance of 2.945 Å lies well within the values for the metal–metal single bond and falls within the expected range for the phosphido- and hydride-bridged complexes such as [(η^5-C_5H_5)(CO)$_2$Mo]$_2$(μ-H)(μ-PMe_2) (3.267 Å)[12a] and $[(PPh_3)(Ph)Pt(\mu$-$H)(\mu$-$PPh_2)Pt(PPh_3)_2]^+$ (2.901 Å).[14] The

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[5] **2**: IR (KBr) 3031, 2997, 2893, 1581, 1483, 1432, 1374, 1021, 749, 741, 699, 522, 489, 474 cm^{-1}; ^1H NMR (C_6D_6) δ −16.6 (d, J_{PH} = 40.6 Hz, 1 H, Ru–H–Ru), 1.87 (s, 30 H, C_5*Me*$_5$), 2.71 (m, 2 H, η^4-C_6H_6), 2.77 (m, 2 H, η^4-C_6H_6), 5.41 (m, 2 H, η^4-C_6H_6), 7.91–6.81 (m, 10 H, PPh_2); ^{13}C NMR (C_6D_6) δ 10.4 (q, J_{CH} = 126.4 Hz, C_5*Me*$_5$), 46.4 (d, J_{CH} = 157.3 Hz, η^4-C_6H_6), 47.8 (d, J_{CH} = 161.3 Hz, η^4-C_6H_6), 93.5 (s, *C*$_5$Me$_5$), 124.3 (dd, J_{PC} = 5.9 Hz, J_{CH} = 158.6 Hz, η^4-C_6H_6), 125.4 (dd, J_{PC} = 8.8 Hz, J_{CH} = 157.3 Hz, P*Ph*$_2$), 126.2 (dd, J_{PC} = 9.8 Hz, J_{CH} = 161.6 Hz, P*Ph*$_2$), 134.7 (dd, J_{PC} = 10.8 Hz, J_{CH} = 154.6 Hz, P*Ph*$_2$), 137.8 (dd, J_{PC} = 7.8 Hz, J_{CH} = 158.6 Hz, P*Ph*$_2$); $^{31}P\{^1H\}$ NMR (C_6D_6 external H_3PO_4) δ 168.0; mp 208 °C dec. Anal. Calcd for $C_{38}H_{47}PRu_2$: C, 61.94; H, 6.42. Found: C, 62.16; H, 6.57.

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[13] Complex **2** crystallized from pentane in the orthorhombic system, space group *Pcab*, with a = 19.612 (2) Å, b = 19.965 (8) Å, c = 17.114 (2) Å, V = 6701.2 (27) Å^3, and Z = 8. Intensity data were collected at 25 °C on a Rigaku AFC-5 diffractometer with graphite-monochromated Mo Kα radiation in the $2° < 2\theta < 60°$ range. Data processing was performed on a FACOM A-70 computer by using R-CRYSTAN structure solving program library obtained from Rigaku Corp. The positions of the metal atoms were determined by direct methods. All other atom positions, except for H18, H19, H20, and hydrogen atoms of C_5Me_5 ligands, were obtained by subsequent difference Fourier synthesis. The position of H18, H19, and H20 were determined by calculation. All non-hydrogen atoms were refined anisotropically by a full-matrix least-squares technique. Hydrogen atoms were refined isotropically. The final R and R_w values are 0.0534 and 0.0532, respectively, for 3864 independent reflections $F_o \geq 5\sigma(F_o)$.

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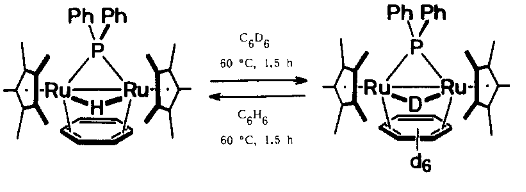
C(4)-C(9) and C(7)-C(8) bond lengths were 1.442 and 1.428 Å, respectively, which were in the range observed for a variety of transition-metal η^2-olefin complexes.[15] By contrast, a C(15)-C(6) distance of 1.332 Å was consistent with that of an isolated carbon-carbon double bond. Some precedent for such bond localization has appeared.[10,16] While C=C and C—C bond lengths of uncoordinated 1,3-butadiene are 1.334 and 1.476 Å, respectively, those in the η^4-diene moiety (C(4)-C(9)-C(8)-C(7)) are 1.435 (average) and 1.460 Å, respectively. The results indicate bond delocalization over the η^4-diene moiety in coordinated benzene as observed in several 1,3-diene complexes.[17] The benzene ring in **2** is nonplanar. The torsional angle between the C(4)-C(9)-C(8)-C(7) plane and the C(4)-C(5)-C(6)-C(7) plane is ca. 12°, and the noncoordinated double bond is bent away from the ruthenium centers.

The formation of **2** would reasonably be elucidated by a sequence of reactions depicted below. Reductive elimination of H_2 from **1** and coordination of PPh_3 would form an intermediary dihydrido monophosphine complex, $(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}H)_2(PPh_3)Ru(\eta^5\text{-}C_5Me_5)$. Activation of the P-C bond of the coordinated PPh_3 by one of the ruthenium centers would be expected to yield the μ-phosphido species $(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}H)_2(\mu\text{-}PPh_2)Ru(C_6H_5)(\eta^5\text{-}C_5Me_5)$, which would then undergo reductive elimination of benzene and subsequent coordination of the benzene in a μ-η^2:η^2-mode to give **2**.

For the cluster-mediated P-C bond cleavage of tertiary phosphine, similar mechanism has been proposed.[18]

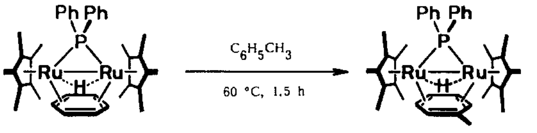
As mentioned above, ^1H NMR study of **2** at the elevated temperature showed that the μ-benzene ligand was not fluxional at least below 80 °C. Slow ligand exchange between μ-benzene and uncoordinated benzene was, however, observed upon heating the benzene solution of **2**. When a solution of **2** in C_6D_6 was warmed at 60 °C for 1.5 h, the deuterated complex **2**-d_7 was formed exclusively (eq 2).



(2)

Complex **2**-d_7 was isolated in 82% yield and was characterized by means of ^2H and ^{13}C NMR and infrared spectroscopy. Resonances for the μ-C_6D_6 and deuteride ligands appeared at δ 5.20 (m, 2 D), 2.77 (m, 2 D), 2.70 (m, 2 D), and −16.5 (d, J_{PD} = 5.0 Hz, 1 D), respectively, in the $^2H\{^1H\}$ NMR spectrum. The $^{13}C\{^1H\}$ NMR spectrum showed three triplets for the μ-C_6D_6 ligand at δ 123.7 (t, J_{CD} = 23.1 Hz), 47.3 (t, J_{CD} = 23.8 Hz), and 45.9 (t, J_{CD} = 22.6 Hz). Coordination of the C_6D_6 molecule was further confirmed on the basis of ν_{CD} bands at 2295, 2281, and 2228 cm^{-1} observed in the infrared spectrum. Treatment of the deuterated complex **2**-d_7 in C_6H_6 at 60 °C for 1.5 h again afforded **2** quantitatively.

Replacement of the coordinated benzene by toluene leading to **3** was also observed by means of ^1H NMR spectroscopy upon heating complex **2** in toluene at 60 °C (eq 3).[19] Monitoring the conversion of **2** or **3** to **2**-d_7 at 60 °C in 10-min intervals by means of ^1H NMR spectroscopy showed that the rate of $Ru_2(C_6H_6)/Ru_2(C_6D_6)$ exchange was comparable to that of $Ru_2(C_6H_5CH_3)/Ru_2(C_6D_6)$ exchange and that the rate of η^4-arene exchange was much faster than that of Ru_2H/Ru_2D exchange.



(3)

These results strongly imply that the conversion of **2** to **2**-d_7 proceeds via initial $Ru_2(C_6H_6)/Ru_2(C_6D_6)$ exchange followed by the cleavage of C-H bond of coordinated benzene.

Further mechanistic studies pertaining to the H/D exchange will be reported in due course.

Acknowledgment. Support from the Ministry of Education, Science and Culture of the Japanese Government (No. 63550618) is gratefully acknowledged.

Supplementary Material Available: Tables of crystallographic data from the X-ray study, atomic coordinates, interatomic distances and angles, and thermal parameters (11 pages); a listing of calculated and observed structure factors (20 pages). Ordering information is given on any current masthead page.

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[19] **3**: ^1H NMR (C_6D_6) δ −16.7 (d, J_{PH} = 40.3 Hz, 1 H, Ru-H-Ru), 1.37 (s, 3 H, $C_6H_5C\mathit{H}_3$), 1.59 (s, 15 H, $C_5\mathit{Me}_5$), 1.67 (s, 15 H, $C_5\mathit{Me}_5$), 2.58 (d, J_{HH} = 7.4 Hz, 1 H, $C_6\mathit{H}_5CH_3$), 2.65 (dd, J_{HH} = 7.4 and 5.5 Hz, 1 H, $C_6\mathit{H}_5CH_3$), 2.76 (dd, J_{HH} = 7.4 and 5.5 Hz, 1 H, $C_6\mathit{H}_5CH_3$), 2.82 (dd, J_{HH} = 7.4 and 5.5 Hz, 1 H, $C_6\mathit{H}_5CH_3$), 5.31 (d, J_{HH} = 5.5 Hz, 1 H, $C_6\mathit{H}_5CH_3$), 6.72–7.76 (m, 10 H, $P\mathit{Ph}_2$); ^{13}C NMR (C_6D_6) δ 10.3 (q, J_{CH} = 126.5 Hz, $C_5\mathit{Me}_5$), 10.6 (q, J_{CH} = 126.2 Hz, $C_5\mathit{Me}_5$), 45.8 (d, J_{CH} = 162.4 Hz, η^4-toluene), 46.2 (d, J_{CH} = 154.6 Hz, η^4-toluene), 48.4 (d, J_{CH} = 153.6 Hz, η^4-toluene), 50.2 (d, J_{CH} = 156.5 Hz, η^4-toluene), 93.3 (s, C_5Me_5), 93.5 (s, C_5Me_5). Resonances for aromatic carbons on PPh_2 and toluene ligands could not be assigned.

First Example of Catalytic Decarbonylation and Metathesis Reactions of α-Ketophosphonates Promoted by a Palladium Complex

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Summary: Arylketophosphonates and alkylketophosphonates undergo decarbonylation in toluene-reflux conditions, in the presence of a catalytic amount of a palladium complex, to afford arylphosphonates and alkylphosphonates, respectively. Evidence is presented for a metathesis reaction of α-ketophosphonates ($RC(O)P(O)(OR)_2 + R'C(O)P(O)(OR')_2 \rightleftharpoons RC(O)P(O)(OR')_2 + R'C(O)P(O)(OR)_2$), catalyzed by a palladium complex, which takes place prior to the observed decarbonylation reaction.

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