Synthesis and Reactions of Terminal Osmium and Ruthenium Complexed Phosphinidenes [(η^6-Ar)(L)M=PMes*]

Arjan T. Termaten,[a] Tom Nijbacker,[a] Marius Schakel,[a] Martin Lutz,[b] Anthony L. Spek,[b] and Koop Lammertsma*[a]

Abstract: Novel, very stable ruthenium and osmium containing terminal phosphinidene complexes [(η^6-Ar)-(L)M=PMes*] (Ar = benzene, *p*-cymene; L = PR_3, CO, and RNC) have been prepared by dehydrohalogenation of novel [(η^6-Ar)MX_2(PH_2Mes*)] complexes in the presence of a stabilizing ligand. X-ray crystal structures are reported for [(η^6-C_6H_6)(PPh_3)Ru=PMes*] (**9**) and [(η^6-*p*Cy)(PPh_3)Os=PMes*] (**4**). Dehydrohalogenation in the absence of a stabilizing ligand resulted in the new P-spiroannulated Ru_2P_2-ring structure **16**. Dehydrohalogenation in the presence of but-2-yne gave a novel phosphaallyl complex [(η^6-Ar)Ru(η^3-R_2PC-(Me)CHMe)] **26**, for which an X-ray crystal structure is reported. The mechanism by which **16** and **26** are obtained is presumed to involve the intermediate formation of the 16-electron (η^6-benzene)Ru=PMes* phosphinidene complex.

Keywords: heterocycles · metallacycles · osmium · P ligands · phosphorus · ruthenium

Introduction

Low-valent organophosphorus reagents have been successfully exploited in the past decades as valuable synthetic tools for rapid access to novel heterocyclic compounds.[1] Particular attention has been given to transition metal complexed phosphinidenes, L_nM=PR.[1, 2, 3] These singly substituted phosphorus compounds require a stabilizing transition metal complex in order to be accessible and useful reagents. Most of the chemistry has concerned the application of [$(CO)_5$W=PR], which enabled the synthesis of a wealth of novel (strained) organophosphorus compounds; the Cr and Mo analogues are also known.[2] These transient reagents, which are generated in situ, have electrophilic properties. Recently, we developed another electrophilic reagent, [$(CO)_4$Fe=PN*i*Pr_2].[4] However, neither of these neutral Fischer-type species has been observed directly, in contrast to the cationic complexes [Cp*$(CO)_3$M=PN(*i*Pr)$_2$]$^+$ (M = Mo, W) and [Cp*$(CO)_2$Ru=PN(*i*Pr)$_2$]$^+$ that were reported recently by Carty et al.[5]

Nucleophilic, Schrock-type phosphinidene complexes display a much higher stability. Since the mid-1980s a number of X-ray structures have been reported for phosphinidenes containing different transition metals (Co, Ir, Mo, Ni, Rh, Ta, U, W, and Zr).[3, 6–8] Notably absent in this series are the Group 8 transition metals Fe, Ru and Os, which sharply contrasts the extensively studied isolobal carbene, imido and oxo complexes.[9] Of these the Ru-based carbene complexes, such as [$(PR_3)_2Cl_2$Ru=CHR],[10] have had a tremendous impact in olefin metathesis reactions. Also the syntheses of stable imido complexes of the type [(η^6-Ar)M≡NR] (M = Ru,[11] Os[12]) have been reported. Their reactivities, such as cycloadditions and dimerizations, were shown to resemble those of the isoelectronic iridium complexes [Cp*Ir≡NR],[13, 14] but to differ from those of, for example, transient zirconium complex [Cp_2Zr=NR].[15]

Recently, we reported on the transient iridium phosphinidene complex, [Cp*Ir≡PAr], which gave stable adducts [Cp*(L)Ir=PAr] with a range of ligands (L = PR_3, $P(OR)_3$, AsR_3, dppe, RN≡C and CO).[7] The other stabilized Group 9 transition metal complexes (Rh and Co) complexes could also be prepared.[8] In this paper, we extend our search for new nucleophilic phosphinidene complexes to those with the Group 8 transition metals Ru and Os.

[a] Prof. Dr. K. Lammertsma, Dr. A. T. Termaten, Ing. T. Nijbacker, Dr. M. Schakel
Department of Organic and Inorganic Chemistry
Faculty of Sciences
Vrije Universiteit, De Boelelaan 1083
1081 HV, Amsterdam (The Netherlands)
Fax: (+31) 20-444-7488
E-mail: lammert@chem.vu.nl

[b] Dr. M. Lutz, Prof. Dr. A. L. Spek
Bijvoet Center for Biomolecular Research
Department of Crystal and Structural Chemistry
Utrecht University, Padualaan 8
3584 CH, Utrecht (The Netherlands)

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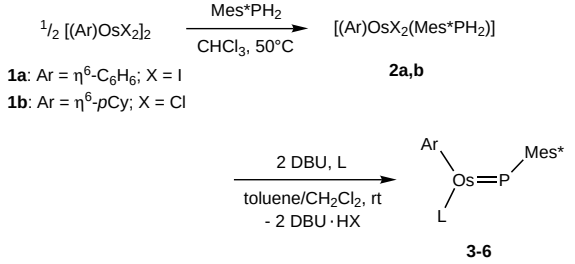
Results and Discussion

The synthetic route toward the Os and Ru containing phosphinidene complexes utilizes a dehydrohalogenation–ligation sequence from appropriately substituted primary phosphine complexes, $[(\eta^6\text{-Ar})MX_2(RPH_2)]$ (M = Os, Ru), in analogy to the syntheses of the earlier reported Co, Rh, and Ir containing isoelectronic and isolobal $[\eta^5\text{-Cp}^R(L)M{=}PAr]$ complexes.[7, 8] The novel precursors can be prepared from $[(\eta^6\text{-Ar})MCl_2]_2$ in which the aromatic group is a benzene ring (labeled **a**) or the sterically more demanding *p*-cymene (*p*Cy, methyl-4-iso-propylphenyl, labeled **b**).

First, the synthesis and characterization of stable osmium phosphinidene complexes $[(\eta^6\text{-Ar})(L)Os{=}PMes^*]$ with CO and PPh_3 ligands will be described, followed by the preparation of the lighter Ru complexes and an investigation of their reactivity.

Osmium phosphinidene complexes $[(\eta^6\text{-Ar})(L)Os{=}PMes^*]$: The required novel osmium containing primary phosphine complexes **2a**, **b** were prepared from the $[(\eta^6\text{-Ar})OsX_2]_2$ dimers **1a**, **b** and 2,4,6-tri-*tert*-butylphenylphosphine Mes^*PH_2 (Scheme 1). Their ^{31}P and ^1H NMR spectra exhibit characteristically large $^1J(P,H)$ coupling constants of 393–395 Hz.[16]



Scheme 1.

The base induced dehydrohalogenation–ligation reaction was explored for **2a**,**b** with two very different ligand systems, PPh_3 and CO. The results are collected in Table 1. Treatment of **2a** with 2 equiv 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in the presence of PPh_3 afforded dark orange crystals of novel complex **3** in 75% yield. The ^{31}P NMR chemical shift at δ 674 is typical for a bent phosphinidene complex[3] and resembles that of previously reported Ir phosphinidene complexes.[7] The same reaction with **2b** yielded **4** (92%), which exhibits a similar ^{31}P NMR resonance at δ 668. The $^2J(P,P)$ coupling constants for **3** (72 Hz) and **4** (80 Hz) suggest in both cases an *E* configuration for both their Os=P bond as the $^2J(P,P)$ value is expected to be much smaller for a *Z* configuration.[7]

A crystal structure determination ascertained the structure of terminal phosphinidene complex **4** and its *E* configuration for the Os=P bond (Figure 1). The two-legged piano stool geometry of the osmium center has a long single Os1–P2 bond of 2.3054(6) Å and a short Os1–P1 one of 2.2195(7) Å that is illustrative of double bond character. The acute P1-Os1-P2 angle of 84.57(3)° and the 106.56(9)° Os1-P1-C1 angle further characterize the bent phosphinidene complex.

Dehydrohalogenation of **2a** in the presence of carbon monoxide also afforded a stable phosphinidene complex **5** (78%), which has a decomposition temperature of 125 °C. The strong $\tilde{\nu}$(CO) IR frequency at 1939 cm^{-1} confirms the presence of a terminal CO ligand and the phosphinidene moiety is evident from its single ^{31}P NMR resonance at δ 731. Based on this chemical shift (see below), we assume an *E* configuration for the Os=P bond. The high solubility of **5** hampered the generation of suitable crystals for X-ray analysis, but its ^1H, ^{13}C, and ^{31}P NMR spectroscopic data are unambiguous, also when compared with **3**, **4**, and the reported [*Z*-Cp*(CO)Ir=PMes*] with its much more deshielded $\delta(^{31}P)$ of 805.[7]

The same reaction with the more congested **2b** afforded phosphinidene **6** as an inseparable 1:1 mixture of *E*/*Z* isomers, which was more difficult to isolate than the other complexes. The lower ^{31}P NMR chemical shift of δ 724 is assigned to the *E*-isomer and the more deshielded one at δ 744 to the *Z*-isomer in accordance with earlier observations.[7] The formation of both isomers is attributed to steric repulsion between the *p*-cymene ligand on Os and the Mes* substituent on P. The CO group is not expected to direct the *E*:*Z* ratio in contrast to the large PPh_3 group present in **3** and **4**. This steric argument supports the assigned *E* configuration for **5**.

Ruthenium phosphinidene complexes $[(\eta^6\text{-Ar})(L)Ru{=}PMes^*]$: Phosphinidenes complexed to transition metals of the second row are generally more reactive than their third row congeners, which encouraged us to explore the properties of the Ru complexes in more detail. The required novel primary phosphine precursor complexes **8a**, **b** were prepared from the commercially available dimers **7a**, **b** and Mes^*PH_2 as described above for the Os complexes (Scheme 2). The results of dehydrohalogenating **8a**,**b** in the presence of ligands PPh_3, PMe_3, CO, and *t*BuNC are summarized in Table 2.

Elimination of HCl from **8a** with DBU in the presence of triphenylphosphine, gave novel phosphinidene complex $[(\eta^6\text{-benzene})(PPh_3)Ru{=}PMes^*]$ (**9**) in 94% yield as high-melting (178–180 °C) dark green crystals with a low field ^{31}P NMR resonance at δ 846 ($^2J(P,P)$ = 40 Hz) that is characteristic for an *E* configuration and analogous to those reported previously for the Rh complexes.[7] With the smaller PMe_3 ligand, instead of PPh_3, stable phosphinidene **11** was obtained also with an *E* configuration as judged by its ^{31}P NMR data

Table 1. Osmium phosphinidene complexes.

Entry	Reactant	L	Product	Yield [%][a]	δ ^{31}P [ppm][b]	$^2J(P,P)$ [Hz]	m.p. [°C][c]
1	**2a**	PPh_3	[(benzene)(PPh_3)Os=PMes*] (**3**)	75	674, 19	72	145
2	**2b**	PPh_3	[(*p*Cy)(PPh_3)Os=PMes*] (**4**)	92	668, 19	80	136
3	**2a**	CO	[(benzene)(CO)Os=PMes*] (**5**)	78	731	–	125
4	**2b**	CO	[(*p*Cy)(CO)Os=PMes*] (**6**)	54	744 (52%)	–	–
					724 (48%)	–	–

[a] Isolated yields. [b] In C_6D_6 as solvent. [c] Or decomposition temperature.

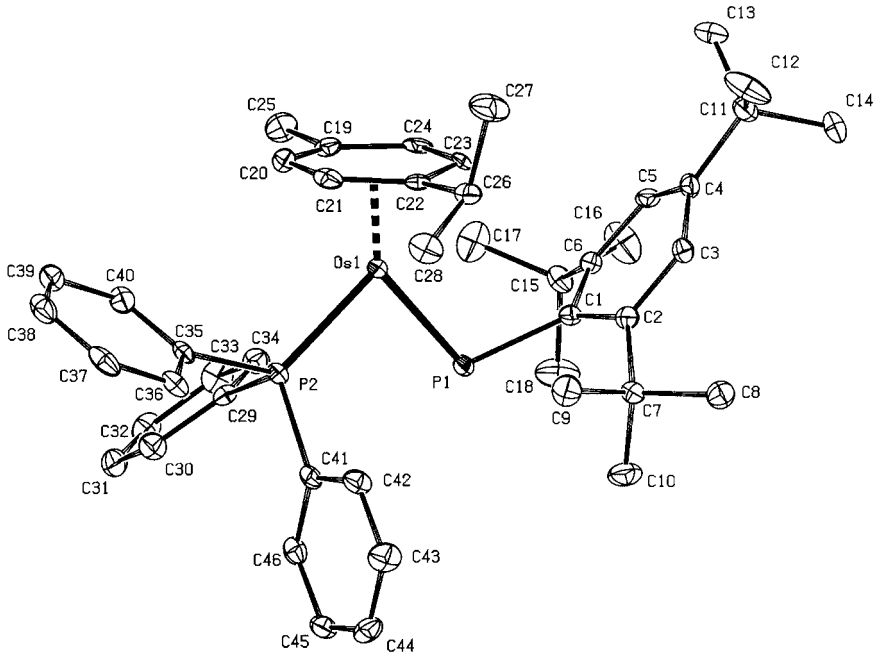
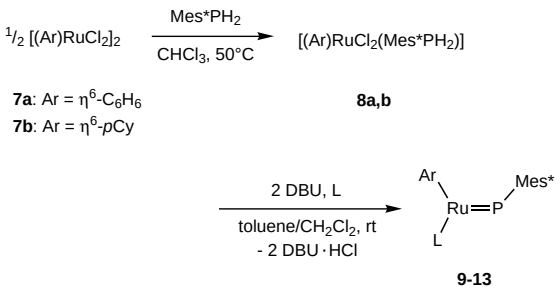


Figure 1. Displacement ellipsoid plot (50% probability level) of **4**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å], angles [°] and torsion angles [°]: Os1–P1 2.2195(7), Os1–P2 2.3054(6), Ar(cg)–Os1 1.7560(11), P1–C1 1.880(3), P2–C29 1.846(4), P2–C35 1.847(2), P2–C41 1.837(4), Os1-P1-C1 106.56(9), P1-Os1-Ar(cg) 142.33(4), P1-Os1-P2 84.57(3), P2-Os1-Ar(cg) 133.05(4), C6-C1-C2-C3 20.5(4), C2-C1-C6-C5 – 20.5(4).



Scheme 2.

(Table 2); as noted, *Z* isomers are expected to have smaller *J*(P,P) coupling constants. Reaction of the more congested **8b**, with a *p*-cymene instead of a benzene ligand, gave with DBU and PPh_3 in high yield stable phosphinidene complex **10** with spectroscopic data that are nearly identical to those of **9**. Both their ^{31}P NMR chemical shifts are considerably deshielded with respect to the Os containing analogues **3** and **4**. Similar differences have been observed for the phosphinidene complexes of both Group 9 [$(Cp^*(PPh_3)M{=}PMes^*]$ with M = Rh, Ir)[7, 8] and Group 6 [$(Cp_2M{=}PMes^*]$ with M = Mo, W)[17] and have been attributed to relativistic effects[18] as the geometrical parameters within each group are very similar.

The X-ray structure of **9** (Figure 2) resembles that of Os analogue **4** and shows an *E* configuration for the 2.1988(6) Å short Ru1–P1 double bond. The difference in length (0.13 Å) of this bond with the Ru1–P2 bond is more pronounced than that for the two Rh–P bonds of [$Cp^*(PPh_3)Rh{=}PMes^*$] (0.07 Å),[7] suggesting a weaker metal–ligand interaction for the Ru complex. The 15.5(3)° distortion from planarity of the Mes* ring of **9** is less pronounced than that of Os analogue **4** (20.5(4)°) due to the difference in steric congestion that results from their respective benzene and *p*-cymene ligands.

Introduction of a CO ligand proved to be more difficult as only a small amount of phosphinidene **12** (< 10%) was detected by its very deshielded ^{31}P NMR resonance at δ 896. The lower stability of Ru complex **12** as compared to Os complex **5** resembles observations made for the [$Cp^*(CO)M{=}PMes^*$] analogues of Group 9, of which an X-ray crystal structure was reported for the Ir complex while the Rh complex remains elusive.[7] In contrast to CO ligation, using instead isoelectronic *t*BuN≡C gave in high yield dark green crystals of phosphinidene complex **13** (m.p. 145 °C), which is evident from the ^{31}P NMR chemical shift at δ 821(s) and the presence of a strong $\tilde{\nu}$(CN) IR frequency at 2101 cm^{-1}. The formation of phosphinidene complexes **12** and **13**, which conceivably occurs on ligation of intermediate [(η^6-Ar)Ru=PR], differs sharply from the behavior of the analogous Ru imido complexes [(η^6-Ar)Ru≡R], which instead react with CO and RN≡C to give isocyanate and carbodiimide complexes, respectively, rather than to form [(η^6-Ar)(L)-Ru=NR].[13] This seeming disparity may have its origin in the difference in N (3.0) and P (2.1) electronegativities, causing the imido group to act as a nucleophile.

Dimerization of phosphinidene complex [(η^6-benzene)-Ru=PMes*]: A question concerning the above discussed

Table 2. Ruthenium phosphinidene complexes.

Entry	Reactant	L	Product	Yield [%][a]	δ ^{31}P [ppm][b]	^2J(P,P) [Hz]	m.p. [°C][c]
1	**8a**	PPh_3	[(benzene)(PPh_3)Ru=PMes*] (**9**)	94	846, 41	40	178
2	**8b**	PPh_3	[(*p*Cy)(PPh_3)Ru=PMes*] (**10**)	89	837, 40	44	141
3	**8a**	PMe_3	[(benzene)(PMe_3)Ru=PMes*] (**11**)	82	801, – 14	37	179
4	**8a**	CO	[(benzene)(CO)Ru=PMes*] (**12**)	< 10	896	–	
5	**8a**	*t*BuNC	[(benzene)(*t*BuNC)Ru=PMes*] (**13**)	84	821	–	145

[a] Isolated yields. [b] In C_6D_6 as solvent. [c] Or decomposition temperature.

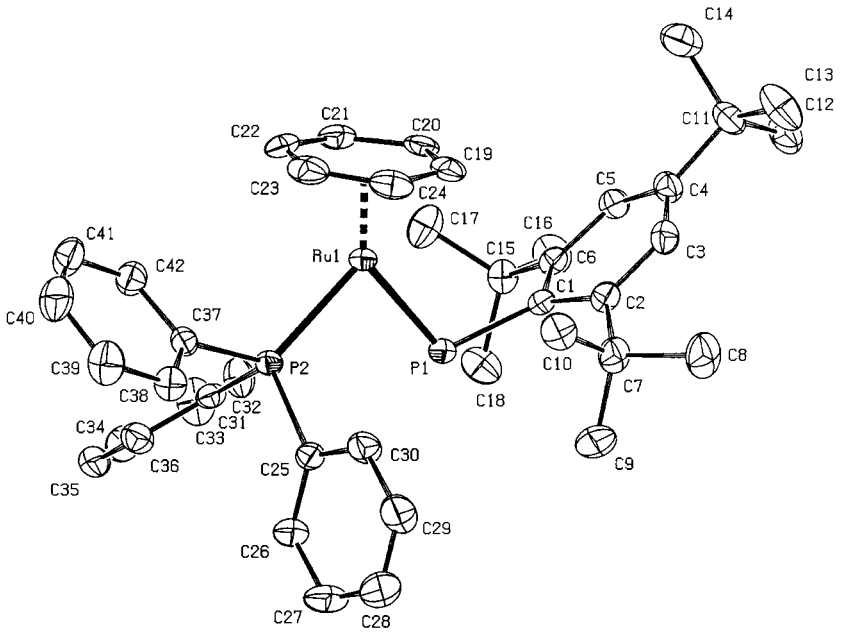


Figure 2. Displacement ellipsoid plot (50% probability level) of $\mathbf{9}\cdot C_5H_{12}$. Hydrogen atoms and *n*-pentane are omitted for clarity. Selected bond lengths [Å], angles [°] and torsion angles [°]: Ru1–P1 2.1988(6), Ru1–P2 2.3289(6), Ar(cg)–Ru1 1.7560(12), P1–C1 1.869(2), P2–C25 1.834(2), P2–C31 1.842(2), P2–C37 1.841(2), Ru1-P1-C1 107.80(7), P1-Ru1-Ar(cg) 140.53(4), P1-Ru1-P2 85.15(2), P2-Ru1-Ar(cg) 134.11(4), C6-C1-C2-C3 15.5(3), C2-C1-C6-C5 –15.0(3).

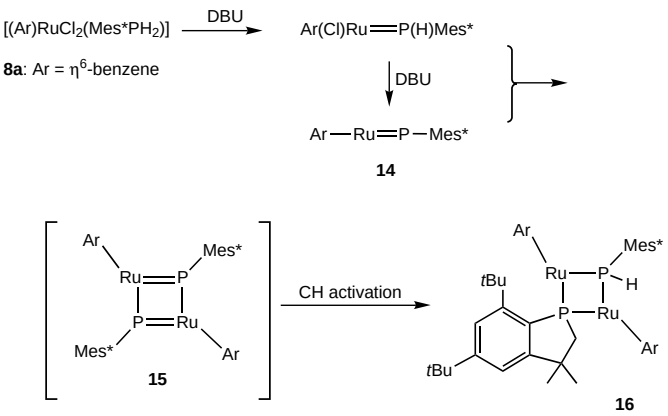
phosphinidene complexes remains the pathway by which they are formed. Presumably, their high stability results (in part) from the additional ligand as no phosphinidene complexes are formed with less stabilizing ligands such as amines, nitriles, and phosphine oxides. We decided to explore in more detail whether a more reactive phosphinidene complex precedes the formation of [(η^6-Ar)(L)Ru=PR].

The first step of this approach was to perform the dehydrohalogenation of **8a** with DBU (2 equiv) in the absence of any coordinating ligand. This resulted in the unexpected formation (in 69%) of an orange-red dimeric product with two nonequivalent phosphorus centers in the ^{31}P NMR spectrum at δ 40.8 ($^1J(P,H) = 356$ Hz) and δ 111 ($^3J(P,H) = 29.9$ Hz), both with a $^2J(P,P)$ coupling constant of 78.2 Hz. These and the presence of nonequivalent *t*Bu groups and new CH_2 and CMe_2 fragments in the ^1H and ^{13}C NMR spectra unequivocally establish structure **16** as the product. Unfortunately, no suitable crystals were obtained for X-ray analysis.

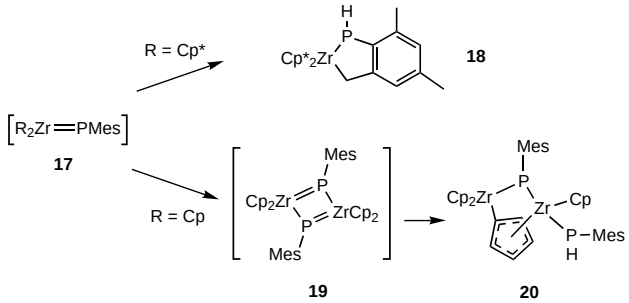
We can only speculate as to the mechanism(s) by which **16** is formed (Scheme 3). Obviously, the first step is the dehydrohalogenation of **8a**. Removal of HCl twice will generate a highly reactive 16-electron phosphinidene complex (**14**),[19] which we presume to dimerize directly to **15**. Alternatively, **14** may react with its precursor, which on removal of HCl also will give **15**. Insertion of one of the P-centers into the neighboring *t*Bu group of its Mes* substituent with simultaneous transfer of a hydrogen to the other P-center of the four-membered ring results in final product **16**. This mechanism shows some resemblance with those that have been proposed to explain the reaction products of the transient zirconium complexed phosphinidenes **17** when no trapping reagents are used (Scheme 4). With Cp* ligands an intramolecular C–H insertion occurs into one of the substituents of the mesityl group to give **18**,[20] but in the less crowded system with Cp ligands a rearranged dimer **20** is formed instead, presumably via [Cp_2Zr=PMes] dimer **19**.[21] Likewise, it is noted that dimers of a phosphinidene tantalum complex **23** are formed when [Cp*$TaCl_4$] **22** is treated with LiPHR, but that a reduction of [Cp*$TaCl_4PH_2R$] towards **21** takes place with DBU (Scheme 5).[22]

Reaction of phosphinidene complex [(η^6-benzene)Ru=PMes*] with 2-butyne: The next step was to explore whether additional support might be obtained for the intermediate formation of a 16-electron [ArRu=PMes*] species by trapping it, before dimerization, with a ligand that is less stabilizing than those that lead to [(η^6-Ar)(L)Ru=PR].

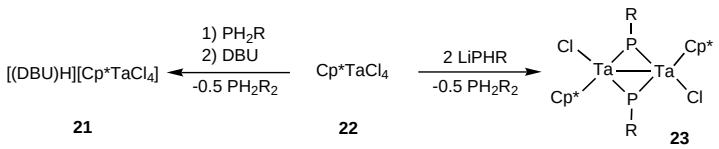
Conducting the dehydrohalogenation of **8a** in the presence of olefin π-acceptors did not give, however, the desired [(η^6-Ar)(η^2-olefin)Ru=PMes*] product, but lead instead to dimer **16**. Trapping with but-2-yne was more successful, but yielded



Scheme 3.



Scheme 4.

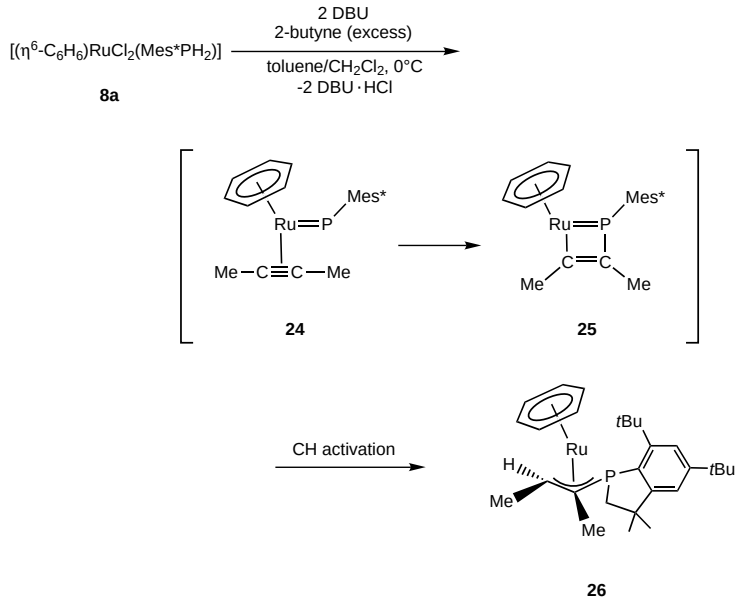


Scheme 5.

(in 77%) an unexpected, air-sensitive orange coloured crystalline product, which, based on its single ^{31}P NMR resonance at δ −4.42, is monomeric and contains no longer a phosphinidene moiety. The two nonequivalent *t*Bu groups, four CH_3 groups, and new CH_2 and CH fragments in the ^{1}H and ^{13}C NMR spectra establish the product as structure **26** (Scheme 6). Apparently, the phosphinidene has inserted into the *ortho t*Bu group of its Mes* substituent with hydrogen transfer to the alkyne group to give a phosphaallyl coordinating ligand. Structure **26** represents a unique example of a neutral, monometallic complex that contains a 4-electon donor phosphaallyl ligand. Such ligands are of interest because of their hemilabile properties and their reactivity towards nucleophiles.[23]

A crystal structure determination confirmed the structure of **26** (Figure 3) with its phosphaindane and phosphaallyl moieties. The structural features of this *neutral* species show resemblance with those of *cationic* Ru phosphaallyl complex [(η^5-Cp)Ru(η^1-dpvp)-(η^3-dpvp)]PF_6 (**27**; dpvp = diphenylvinylphosphine)[24] with subtle but important differences for the Ru–η^3-phosphaallyl interaction. Namely, the Ru1−P1 bond (2.2361(8) Å) is shorter than in **27** (2.276(1) Å) and its two Ru1−C2 and Ru1−C3 distances are of equal length (2.170(3) and 2.177(3) Å, respectively), whereas they differ significantly for **27** (2.176(3) and 2.244(4) Å, respectively). Evidently, **26** binds the phosphaallyl ligand more tightly. The allylic unit itself with P1−C2 and C2−C3 bond lengths of 1.775(3) and 1.437(4) Å, respectively, is similar to those reported for **27** and the Co[25] and Mo[26] phosphaallyl complexes **28** and **29**, respectively (Scheme 7), but the P1-C2-C3 angle of 107.4(2) is rather small.

We speculate that the formation of **26** starts by ligating initially formed **14** with but-2-yne to give **24**, followed by



Scheme 6.

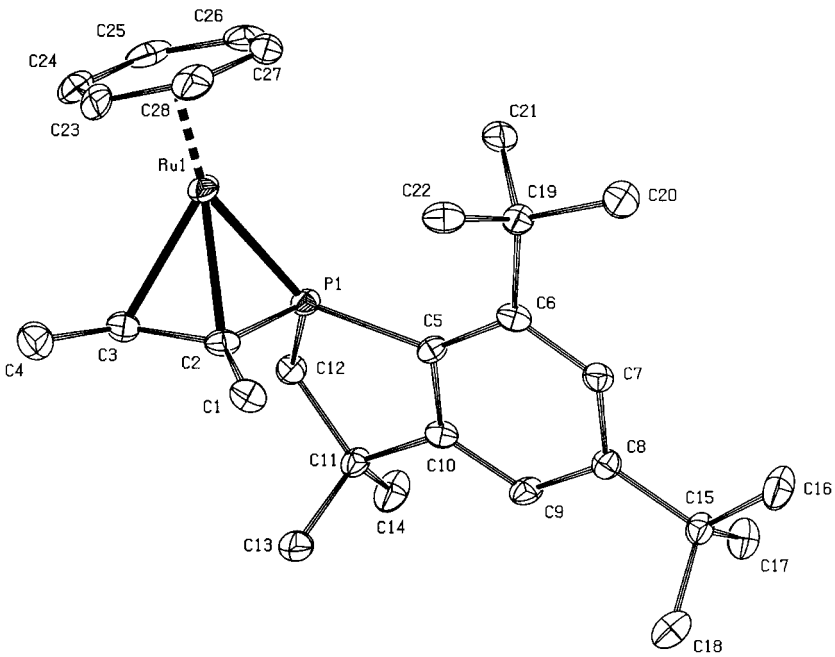
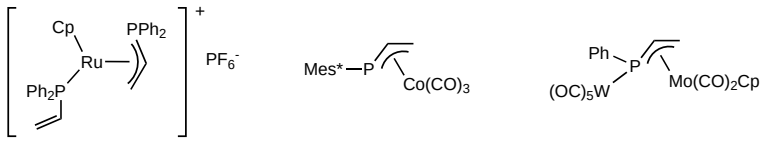


Figure 3. Displacement ellipsoid plot (50% probability level) of **26**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å], angles [°] and torsion angles [°]: Ru1−P1 2.2361(8), Ru1−Ar(cg) 1.7302(14), Ru1−C2 2.170(3), Ru1−C3 2.177(3), C1−C2 1.509(4), C2−C3 1.437(4), C3−C4 1.513(4), P1−C2 1.775(3), P1−C5 1.850(3), P1−C12 1.832(3), C11−C12 1.542(4), C11−C13 1.535(4), C11−C14 1.535(4), Ru1-C3-C4 118.9(2), Ru1-C2-C1 131.8(2), Ru1-P1-C2 64.32(10), Ru1-P1-C5 140.32(9), Ru1-P1-C12 127.02(10), C1-C2-C3 125.0(3), C2-C3-C4 120.0(3), P1-C2-C1 127.2(2), P1-C2-C3 107.4(2), P1-C12-C11 107.51(19), C10-C11-C12 105.2(2), C13-C11-C14 110.3(3), C5-C10-C11 118.1(3), P1-C5-C10 107.6(2), C5-P1-C12 91.59(13), C2-P1-C5 112.88(14), C2-P1-C12 112.72(14), P1-C2-C3-C4 −171.5(2), P1-C5-C10-C11 5.2(3), C5-P1-C12-C11 29.8(2).



27 28 29

Scheme 7.

cyclization to the four-membered ring structure **25**, which subsequently undergoes an intramolecular C–H insertion of the P-center into an *ortho* *t*Bu group with concurrent hydrogen transfer to an olefinic carbon (Scheme 6). This mechanism is analogous to that proposed for the dimerization, but whereas metallacycle **25** ring opens upon H-transfer, dimetallacycle **15** does not.

Conclusion

In this study, the synthesis and characterization of novel Group 8 transition metal phosphinidene complexes [(η^6-Ar)(L)M=PMes*] (M = Ru, Os; L = PR_3, CO, and RNC; Ar = benzene, *p*-cymene) are described. Their synthesis involves a dehydrohalogenation–ligation sequence starting from novel primary phosphine complexes][(η^6-Ar)MX_2-(PH_2Mes*)] X-ray crystal structures are reported for [(η^6-*p*Cy)(PPh_3)Os=PMes*] (**4**) and [(η^6-C_6H_6)(PPh_3)Ru=PMes*] (**9**).

The dehydrohalogenation reaction of Ru complex **8a** in the absence of a stabilizing ligand yields dimeric **16**. This is speculated to result from dimerization of an initially formed 16-electron [(η^6-benzene)Ru=PMes*] complex, followed by insertion of the P-center into a *t*Bu group of its Mes* substituent with concurrent H-transfer to the other P-center.

Dehydrohalogenation of **8a** in the presence of but-2-yne affords novel phosphaallyl complex **26**, presumably by a similar reaction mechanism, suggesting that the 16-electron (η^6-benzene)Ru=PMes* complex activates the alkyne group.

Experimental Section

General remarks: All experiments were performed in flame-dried glassware and under an atmosphere of dry nitrogen or argon. Solvents were distilled (under N_2) from sodium (toluene), sodium/benzophenone (THF), diphosphoruspentoxide (CH_2Cl_2, $CHCl_3$) or lithium aluminum hydride (*n*-pentane). Deuterated solvents were dried over 4 Å molecular sieves ($CDCl_3$, C_6D_6). All solid starting materials were dried in vacuo. NMR spectra were recorded on a Bruker Avance 250 spectrometer at 250.13 (^{1}H), 62.90 (^{13}C) and 101.3 (^{31}P) MHz, or on a Bruker Avance 400 spectrometer at 400.13 (^{1}H) and 100.64 (^{13}C) MHz. ^{1}H NMR spectra were referenced to $CHCl_3$ (δ 7.27 ppm) or C_6D_5H (δ 7.17 ppm), ^{13}C NMR spectra to $CDCl_3$ (δ 77.16 ppm) or C_6D_6 (δ 128.06 ppm) and ^{31}P NMR spectra to external 85% H_3PO_4. IR spectra were recorded on a Mattson-6030 Galaxy FTIR spectrophotometer, and high-resolution mass spectra (HRMS) on a Finnigan Mat 900 spectrometer. Elemental analyses were performed by Mikroanalytisches Labor Pascher, Remagen-Bandorf (Germany). [(η^6-C_6H_6)OsI_2]$_2$,[27] [(η^6-*p*Cy)$OsCl_2$]$_2$,[28] Mes*PH_2,[29] were prepared according to literature procedures. [(η^6-C_6H_6)$RuCl_2$]$_2$ and [(η^6-*p*Cy)$RuCl_2$]$_2$ were purchased from Aldrich and used as received.

[(η^6-C_6H_6)OsI_2(PH_2Mes*)] (2a): Mes*PH_2 (0.31 g, 1.10 mmol) was added to a yellow-brown solution of [(η^6-C_6H_6)OsI_2]$_2$ (0.52 g, 0.50 mmol) in $CHCl_3$ (50 mL), which was stirred for 3 h at 50 °C and filtered to remove insoluble material. After concentrating the solution to a few mL, *n*-pentane (30 mL) was added slowly to cause precipitation of an orange powder, which was isolated by filtration, washed with *n*-pentane (25 mL), and dried in vacuo. Recrystallization from CH_2Cl_2/*n*-pentane yielded **2a** as orange needles (0.67 g, 0.84 mmol, 84%). M.p. > 225 °C (decomp); ^{1}H NMR (250.13 MHz, $CDCl_3$, 300 K): δ = 1.36 (s, 9H, *p*-C(CH_3)$_3$), 1.57 (s, 18H, *o*-C(CH_3)$_3$), 5.29 (s, 6H, C_6H_6), 7.58 (d, ^4J(P,H) = 2.4 Hz, 2H, *m*-Mes*), 7.67 (d, ^1J(P,H) = 395 Hz, 2H, PH_2); ^{13}C{^{1}H} NMR (62.90 MHz, $CDCl_3$, 300 K): δ = 31.2 (s, *p*-C(CH_3)$_3$), 33.6 (s, *o*-C(CH_3)$_3$), 35.3 (s, *p*-*C*(CH_3)$_3$), 38.4 (d, ^3J(P,C) = 2.3 Hz, *o*-*C*(CH_3)$_3$), 80.5 (d, ^2J(P,C) = 3.6 Hz, C_6H_6), 122.4 (d, ^3J(P,C) = 9.8 Hz, *m*-Mes*), 125.2 (d, ^1J(P,C) = 41.5 Hz, *i*-Mes*), 152.7 (brs, *p*-Mes*), 155.0 (d, ^2J(P,C) = 5.4 Hz, *o*-Mes*); ^{31}P NMR (101.3 MHz, $CDCl_3$, 300 K): δ = −77.4 (t, ^1J(P,H) = 395 Hz); IR (KBr): $\tilde{\nu}$(PH) = 2319, 2411 cm^{-1}; HRMS: calcd for $C_{24}H_{37}PI_2Os$: 802.03375; found: 802.03664.

[(η^6-*p*Cy)$OsCl_2$(PH_2Mes*)] (2b): In a fashion similar to that described for **2a**, [(η^6-*p*Cy)$OsCl_2$]$_2$ (0.79 g, 1.00 mmol) and Mes*PH_2 (0.58 g, 2.10 mmol) were used to give yellow crystals of **2b** (0.85 g, 1.26 mmol, 63%). M.p. 172–173 °C (decomp; CH_2Cl_2); ^{1}H NMR (250.13 MHz, $CDCl_3$, 300 K): δ = 1.22 (d, ^3J(H,H) = 6.9 Hz, 6H, CH(CH_3)$_2$), 1.35 (s, 9H, *p*-C(CH_3)$_3$), 1.50 (s, 3H, CH_3), 1.53 (s, 18H, *o*-C(CH_3)$_3$), 2.64 (septet, ^3J(H,H) = 6.9 Hz, 1H, CH(CH$_3$)$_2$), 5.06 (d, ^3J(H,H) = 5.2 Hz, 2H, C_6H_4), 5.35 (d, ^3J(H,H) = 5.3 Hz, 2H, C_6H_4), 6.54 (d, ^1J(P,H) = 393 Hz, 2H, PH_2), 7.54 (d, ^4J(P,H) = 1.6 Hz, 2H, *m*-Mes*); ^{13}C{^{1}H} NMR (62.90 MHz, $CDCl_3$, 300 K): δ = 17.9 (s, CH_3), 22.6 (s, CH(*C*H$_3$)$_2$), 30.3 (s, *C*H(CH$_3$)$_2$), 31.3 (s, *p*-C(*C*H$_3$)$_3$), 33.4 (s, *o*-C(*C*H$_3$)$_3$), 35.2 (s, *p*-*C*(CH$_3$)$_3$), 38.5 (s, *o*-*C*(CH$_3$)$_3$), 76.3 (s, C_6H_4), 77.4 (d, ^2J(P,C) = 4.6 Hz, C_6H_4), 91.3 (s, C_6H_4), 105.8 (d, ^2J(P,C) = 5.8 Hz, C_6H_4), 120.3 (d, ^1J(P,C) = 40.7 Hz, *i*-Mes*), 122.8 (d, ^3J(P,C) = 9.6 Hz, *m*-Mes*), 152.6 (s, *p*-Mes*), 155.4 (d, ^2J(P,C) = 5.3 Hz, *o*-Mes*); ^{31}P NMR (101.3 MHz, $CDCl_3$, 300 K): δ = −54.9 (t, ^1J(P,H) = 393 Hz); IR (KBr): $\tilde{\nu}$(PH) = 2371, 2419 cm^{-1}. The compound tenaciously holds solvent (CH_2Cl_2, *n*-pentane, toluene; visible in the NMR spectra) after recrystallization, in this case toluene; elemental analysis calcd (%) for $C_{28}H_{45}PCl_2Os \cdot 0.35C_7H_8$: C 51.80, H 6.83, P 4.39; found: C 51.75, H 6.84, P 4.02.

[(η^6-C_6H_6)(PPh_3)Os=PMes*] (3): A red-brown solution of **2a** (160 mg, 0.20 mmol) in CH_2Cl_2 (2.5 mL) was added dropwise to a solution of DBU (59.8 μL, 0.40 mmol) and PPh_3 (52.5 mg, 0.20 mmol) in toluene (5 mL), and stirred for an additional 5 min. After removal of the solvents the residue was extracted with toluene (10 mL), filtered, and concentrated. Addition of *n*-pentane and cooling at −20 °C yielded dark orange crystals of **3** (121 mg, 0.150 mmol, 75%). M.p. > 145 °C (decomp); ^{1}H NMR (250.13 MHz, C_6D_6, 300 K): δ = 1.58 (s, 9H, *p*-C(CH_3)$_3$), 1.71 (s, 18H, *o*-C(CH_3)$_3$), 4.66 (s, 6H, C_6H_6), 7.13–7.24 (m, 9H, PPh_3), 7.55 (s, 2H, *m*-Mes*), 7.93–8.00 (m, 6H, PPh_3); ^{13}C{^{1}H} NMR (62.90 MHz, C_6D_6, 300 K): δ = 32.0 (s, *p*-C(*C*H$_3$)$_3$), 32.5 (d, ^4J(P,C) = 6.8 Hz, *o*-C(*C*H$_3$)$_3$), 34.7 (s, *p*-*C*(CH$_3$)$_3$), 38.2 (s, *o*-*C*(CH$_3$)$_3$), 77.5 (d, ^2J(P,C) = 3.2 Hz, C_6H_6), 119.2 (s, *m*-Mes*), 127.5 (d, ^3J(P,C) = 9.9 Hz, *m*-PPh_3), 129.4 (d, ^4J(P,C) = 2.0 Hz, *p*-PPh_3), 135.5 (d, ^2J(P,C) = 10.8 Hz, *o*-PPh_3), 139.8 (d, ^1J(P,C) = 50.5 Hz, *i*-PPh_3), 145.8 (s, *p*-Mes*), 146.8 (s, *o*-Mes*), 177.5 (dd, ^1J(P,C) = 106.4 Hz, ^3J(P,C) = 18.2, *i*-Mes*); ^{31}P NMR (101.3 MHz, C_6D_6, 300 K): δ = 673.6 (d, ^2J(P,P) = 72 Hz, Os=P), 19.4 (d, ^2J(P,P) = 72Hz, Os-*P*Ph_3); HRMS: calcd for $C_{42}H_{50}P_2Os$: 808.30023; found: 808.30126.

[(η^6-*p*Cy)(PPh_3)Os=PMes*] (4): In a fashion similar to that described for **3**, **2b** (135 mg, 0.20 mmol), DBU (59.8 μL, 0.40 mmol) and PPh_3 (52.5 mg, 0.20 mmol) were used to give dark red crystals of **4** (158 mg, 0.183 mmol, 92%). M.p. > 136 °C (decomp); ^{1}H NMR (250.13 MHz, C_6D_6, 300 K): δ = 0.99 (d, ^3J(H,H) = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.53 (s, 9H, *p*-C(CH_3)$_3$), 1.69 (s, 18H, *o*-C(CH_3)$_3$), 1.91 (s, 3H, CH_3), 2.40 (septet, ^3J(H,H) = 6.8 Hz, 1H, CH(CH$_3$)$_2$), 4.56 (d, ^3J(H,H) = 5.9 Hz, 2H, C_6H_4), 4.60 (d, ^3J(H,H) = 5.8 Hz, 2H, C_6H_4), 7.06–7.20 (m, 9H, PPh_3), 7.47 (s, 2H, *m*-Mes*), 7.89–7.96 (m, 6H, PPh_3); ^{13}C{^{1}H} NMR (62.90 MHz, C_6D_6, 300 K): δ = 19.4 (s, *C*H$_3$), 24.4 (s, CH(*C*H$_3$)$_2$), 31.1 (s, *C*H(CH$_3$)$_2$), 32.1 (s, *p*-C(*C*H$_3$)$_3$), 33.1 (d, ^4J(P,C) = 5.5 Hz, *o*-C(*C*H$_3$)$_3$), 34.7 (s, *p*-*C*(CH$_3$)$_3$), 38.5 (s, *o*-*C*(CH$_3$)$_3$), 79.3

(d, ^2J(P,C) = 3.6 Hz, C_6H_4), 82.1 (d, ^2J(P,C) = 3.5 Hz, C_6H_4), 83.0 (s, C_6H_4), 96.5 (s, C_6H_4), 118.8 (s, *m*-Mes*), 127.4 (d, ^3J(P,C) = 9.8 Hz, *m*-PPh_3), 129.3 (s, *p*-PPh_3), 135.6 (d, ^2J(P,C) = 10.6 Hz, *o*-PPh_3), 140.1 (d, ^1J(P,C) = 49.7 Hz, *i*-PPh_3), 145.4 (s, *p*-Mes*), 146.9 (s, *o*-Mes*), 178.6 (dd, ^1J(P,C) = 109.6 Hz, ^3J(P,C) = 19.6, *i*-Mes*); ^{31}P NMR (101.3 MHz, C_6D_6, 300 K): δ = 667.5 (d, ^2J(P,P) = 80 Hz, Os=P), 18.8 (d, ^2J(P,P) = 80 Hz, Os-*P*Ph_3); HRMS: calcd for $C_{46}H_{58}P_2Os$: 864.36285; found: 864.36078.

[(η^6-C_6H_6)(CO)Os=PMes*] (5): In a fashion similar to that described for **3**, **2a** (160 mg, 0.20 mmol), DBU (59.8 μL, 0.40 mmol), and carbon monoxide (which was passed through the reaction mixture) were used to give deep orange-red crystals of **5** (89 mg, 0.155 mmol, 78 %). M.p. > 125 °C (decomp); ^{1}H NMR (250.13 MHz, C_6D_6, 300 K): δ = 1.39 (s, 9H, *p*-C(CH_3)$_3$), 1.52 (s, 18H, *o*-C(CH_3)$_3$), 4.71 (s, 6H, C_6H_6), 7.31 (s, 2H, *m*-Mes*); ^{13}C{^{1}H} NMR (62.90 MHz, C_6D_6, 300 K): δ = 31.8 (s, *p*-C(*C*H_3)$_3$), 33.0 (d, ^4J(P,C) = 8.0 Hz, *o*-C(*C*H_3)$_3$), 34.7 (s, *p*-*C*(CH_3)$_3$), 38.2 (s, *o*-*C*(CH_3)$_3$), 85.0 (s, C_6H_6), 119.3 (s, *m*-Mes*), 147.2 (s, *p*-Mes*), 147.2 (s, *o*-Mes*), 173.6 (d, ^1J(P,C) = 102.4 Hz, *i*-Mes*), 186.2 (s, *C*O); ^{31}P NMR (101.3 MHz, C_6D_6, 300 K): δ = 731.1 (s, Os=*P*); IR (KBr): $\tilde{\nu}$(CO) = 1939 cm^{-1}; HRMS: calcd for $C_{25}H_{35}OPOs$: 574.20404; found: 574.20014.

[(η^6-*p*Cy)(CO)Os=PMes*] (6): In a fashion similar to that described for **3**, **2b** (135 mg, 0.20 mmol), DBU (59.8 μL, 0.40 mmol), and carbon monoxide (which was passed through the reaction mixture) were used to give **6** as an orange-red powder (68 mg, 0.108 mmol, 54 %). The product proved to be an inseparable mixture of *E*/*Z* isomers that could not be further purified due to high solubility. *E*-**6** (48 %): ^{31}P NMR (101.3 MHz, C_6D_6, 300 K): δ = 723.9 (s, Os=*P*); *Z*-**6** (52 %): ^{31}P NMR (101.3 MHz, C_6D_6, 300 K): δ = 744.4 (s, Os=*P*).

[(η^6-C_6H_6)$RuCl_2$(PH_2Mes*)] (8a): In a fashion similar to that described for **2a**, [(η^6-C_6H_6)$RuCl_2$]$_2$ (0.50 g, 1.00 mmol) and Mes*PH_2 (0.58 g, 2.10 mmol) were used to give orange-yellow crystals of **8a** (0.88 g, 1.67 mmol, 84 %). M.p. > 190 °C (decomp); ^{1}H NMR (250.13 MHz, $CDCl_3$, 300 K): δ = 1.38 (s, 9H, *p*-C(CH_3)$_3$), 1.59 (s, 18H, *o*-C(CH_3)$_3$), 5.17 (s, 6H, C_6H_6), 6.32 (d, ^1J(P,H) = 392 Hz, 2H, PH_2), 7.61 (d, ^4J(P,H) = 2.8 Hz, 2H, *m*-Mes*); ^{13}C{^{1}H} NMR (62.90 MHz, $CDCl_3$, 300 K): δ = 30.9 (s, *p*-C(*C*H_3)$_3$), 32.8 (d, ^4J(P,C) = 1.2 Hz, *o*-C(*C*H_3)$_3$), 35.2 (s, *p*-*C*(CH_3)$_3$), 38.3 (d, ^3J(P,C) = 2.3 Hz, *o*-*C*(CH_3)$_3$), 87.8 (d, ^2J(P,C) = 3.8 Hz, C_6H_6), 122.3 (d, ^1J(P,C) = 34.7 Hz, *i*-Mes*), 122.6 (d, ^3J(P,C) = 10.0 Hz, *m*-Mes*), 152.8 (d, ^4J(P,C) = 3.4 Hz, *p*-Mes*), 154.4 (d, ^2J(P,C) = 5.6 Hz, *o*-Mes*); ^{31}P NMR (101.3 MHz, $CDCl_3$, 300 K): δ = −22.1 (t, ^1J(P,H) = 392 Hz); IR (KBr): $\tilde{\nu}$(PH) = 2409, 2456 cm^{-1}; elemental analysis calcd (%) for $C_{24}H_{37}PCl_2Ru$: C 54.54, H 7.06, P 5.86; found: C 54.20, H 6.96, P 5.79.

[(η^6-*p*Cy)$RuCl_2$(PH_2Mes*)] (8b): In a fashion similar to that described for **2a**, [(η^6-*p*Cy)$RuCl_2$]$_2$ (0.61 g, 1.00 mmol) and Mes*PH_2 (0.58 g, 2.10 mmol) were used to give orange crystals of **8b** (1.03 g, 1.76 mmol, 88 %). M.p. 165 °C; ^{1}H NMR (250.13 MHz, $CDCl_3$, 300 K): δ = 1.25 (d, ^3J(H,H) = 6.9 Hz, 6H, CH(CH_3)$_2$), 1.37 (s, 9H, *p*-C(CH_3)$_3$), 1.43 (s, 3H, CH_3), 1.57 (s, 18H, *o*-C(CH_3)$_3$), 2.78 (septet, ^3J(H,H) = 6.9 Hz, 1H, CH(CH$_3$)$_2$), 4.84 (d, ^3J(H,H) = 5.8 Hz, 2H, C_6H_4), 5.24 (d, ^3J(H,H) = 5.8 Hz, 2H, C_6H_4), 6.28 (d, ^1J(P,H) = 387 Hz, 2H, PH_2), 7.57 (d, ^4J(P,H) = 2.6 Hz, 2H, *m*-Mes*); ^{13}C{^{1}H} NMR (62.90 MHz, $CDCl_3$, 300 K): δ = 17.5 (s, *C*H_3), 22.2 (s, CH(*C*H_3)$_2$), 30.2 (s, *C*H(CH$_3$)$_2$), 31.0 (s, *p*-C(*C*H_3)$_3$), 33.1 (d, ^4J(P,C) = 1.3 Hz, *o*-C(*C*H_3)$_3$), 35.1 (s, *p*-*C*(CH_3)$_3$), 38.3 (d, ^3J(P,C) = 2.2 Hz, *o*-*C*(CH_3)$_3$), 84.5 (d, ^2J(P,C) = 2.3 Hz, C_6H_4), 85.5 (d, ^2J(P,C) = 5.0 Hz, C_6H_4), 98.6 (s, C_6H_4), 112.2 (d, ^2J(P,C) = 6.3 Hz, C_6H_4), 120.3 (d, ^1J(P,C) = 31.0 Hz, *i*-Mes*), 122.7 (d, ^3J(P,C) = 9.6 Hz, *m*-Mes*), 152.2 (d, ^4J(P,C) = 3.3 Hz, *p*-Mes*), 155.1 (d, ^2J(P,C) = 5.5 Hz, *o*-Mes*); ^{31}P NMR (101.3 MHz, $CDCl_3$, 300 K): δ = −28.0 (t, ^1J(P,H) = 387 Hz); IR (KBr): $\tilde{\nu}$(PH) = 2423, 2344 cm^{-1}; elemental analysis calcd (%) for $C_{28}H_{45}PCl_2Ru$: C 57.52, H 7.76, P 5.30; found: C 57.27, H 7.77, P 5.12.

[(η^6-C_6H_6)(PPh_3)Ru=PMes*] (9): A red-brown solution of **8a** (106 mg, 0.20 mmol) in CH_2Cl_2 (2.5 mL) was added dropwise to a solution of DBU (59.8 μL, 0.40 mmol) and PPh_3 (52.5 mg, 0.20 mmol) in toluene (5 mL), and stirred for an additional 5 min. After removal of the solvents the residue was extracted with *n*-pentane (25 mL), filtered, and concentrated. Cooling at −20 °C yielded green-black crystals of **9** (135 mg, 0.188 mmol, 94 %). M.p. 178–180 °C; ^{1}H NMR (250.13 MHz, C_6D_6, 300 K): δ = 1.51 (s, 9H, *p*-C(CH_3)$_3$), 1.55 (s, 18H, *o*-C(CH_3)$_3$), 4.52 (s, 6H, C_6H_6), 7.08–7.17 (m, 9H, PPh_3), 7.51 (s, 2H, *m*-Mes*), 7.86–7.94 (m, 6H, PPh_3); ^{13}C{^{1}H} NMR (62.90 MHz, C_6D_6, 300 K): δ = 31.9 (s, *p*-C(*C*H_3)$_3$), 32.4 (d, ^4J(P,C) = 4.5 Hz, *o*-C(*C*H_3)$_3$), 34.9 (s, *p*-*C*(CH_3)$_3$), 38.4 (s, *o*-*C*(CH_3)$_3$), 83.9 (d, ^2J(P,C) = 2.2 Hz, C_6H_6), 119.7 (s, *m*-Mes*), 127.7 (d, ^3J(P,C) = 9.4 Hz, *m*-PPh_3), 129.1 (d, ^4J(P,C) = 1.8 Hz, *p*-PPh_3), 135.2 (d, ^2J(P,C) = 11.6 Hz, *o*-PPh_3), 139.5 (d, ^1J(P,C) = 39.0 Hz, *i*-PPh_3), 145.8 (s, *o*-Mes*), 146.1 (s, *p*-Mes*); ^{31}P NMR (101.3 MHz, C_6D_6, 300 K): δ = 845.9 (d, ^2J(P,P) = 40 Hz, Ru=*P*), 40.7 (d, ^2J(P,P) = 40 Hz, Ru-*P*Ph_3); HRMS: calcd for $C_{42}H_{50}P_2Ru$: 718.24304; found: 718.24398.

[(η^6-*p*Cy)(PPh_3)Ru=PMes*] (10): In a fashion similar to that described for **9**, **8b** (117 mg, 0.20 mmol), DBU (59.8 μL, 0.40 mmol) and PPh_3 (52.5 mg, 0.20 mmol) were used to give large dark green crystals of **10** (138 mg, 0.178 mmol, 89 %). M.p. 141–143 °C; ^{1}H NMR (250.13 MHz, C_6D_6, 300 K): δ = 0.93 (d, ^3J(H,H) = 6.9 Hz, 6H, CH(CH_3)$_2$), 1.53 (s, 9H, *p*-C(CH_3)$_3$), 1.61 (s, 18H, *o*-C(CH_3)$_3$), 1.77 (s, 3H, CH_3), 2.40 (septet, ^3J(H,H) = 6.9 Hz, 1H, CH(CH$_3$)$_2$), 4.55 (d, ^3J(H,H) = 6.3 Hz, 2H, C_6H_4), 4.61 (d, ^3J(H,H) = 6.3 Hz, 2H, C_6H_4), 7.03–7.16 (m, 9H, PPh_3), 7.52 (s, 2H, *m*-Mes*), 7.89–7.97 (m, 6H, PPh_3); ^{13}C{^{1}H} NMR (62.90 MHz, C_6D_6, 300 K): δ = 19.0 (s, *C*H_3), 24.3 (s, CH(*C*H_3)$_2$), 30.8 (s, *C*H(CH$_3$)$_2$), 32.0 (s, *p*-C(*C*H_3)$_3$), 32.9 (br s, *o*-C(*C*H_3)$_3$), 34.9 (s, *p*-*C*(CH_3)$_3$), 38.7 (s, *o*-*C*(CH_3)$_3$), 84.6 (d, ^2J(P,C) = 3.2 Hz, C_6H_4), 87.2 (d, ^2J(P,C) = 3.0 Hz, C_6H_4), 91.6 (s, C_6H_4), 105.1 (s, C_6H_4), 119.4 (s, *m*-Mes*), 127.6 (d, ^3J(P,C) = 7.6 Hz, *m*-PPh_3), 129.1 (d, ^4J(P,C) = 1.8 Hz, *p*-PPh_3), 135.3 (d, ^2J(P,C) = 11.4 Hz, *o*-PPh_3), 139.7 (d, ^1J(P,C) = 38.0 Hz, *i*-PPh_3), 145.7 (s, *p*-Mes*), 145.9 (s, *o*-Mes*), 175.2 (dd, ^1J(P,C) = 113 Hz, ^3J(P,C) = 16.6, *i*-Mes*); ^{31}P NMR (101.3 MHz, C_6D_6, 300 K): δ = 837.3 (d, ^2J(P,P) = 44 Hz, Ru=P), 40.1 (d, ^2J(P,P) = 44 Hz, Ru-*P*Ph_3); HRMS: calcd for $C_{46}H_{58}P_2Ru$ 774.30566; found 774.30783.

[(η^6-C_6H_6)(PMe_3)Ru=PMes*] (11): In a fashion similar to that described for **9**, **8a** (106 mg, 0.20 mmol), DBU (59.8 μL, 0.40 mmol) and PMe_3 (0.20 mL of a 1.0 M solution in toluene, 0.20 mmol) were used to give dark green crystals of **11** (87 mg, 0.164 mmol, 82 %). M.p. 179–180 °C; ^{1}H NMR (250.13 MHz, C_6D_6, 300 K): δ = 1.48 (d, ^2J(P,H) = 8.2 Hz, 9H, PMe_3), 1.52 (s, 9H, *p*-C(CH_3)$_3$), 1.66 (s, 18H, *o*-C(CH_3)$_3$), 4.62 (s, 6H, C_6H_6), 7.51 (s, 2H, *m*-Mes*); ^{13}C{^{1}H} NMR (62.90 MHz, C_6D_6, 300 K): δ = 22.5 (dd, ^1J(P,C) = 28.2 Hz, ^3J(P,C) = 9.7 Hz, PMe_3), 31.9 (s, *p*-C(*C*H$_3$)$_3$), 32.8 (d, ^4J(P,C) = 7.9 Hz, *o*-C(*C*H$_3$)$_3$), 34.9 (s, *p*-*C*(CH$_3$)$_3$), 38.5 (s, *o*-*C*(CH$_3$)$_3$), 81.8 (d, ^2J(P,C) = 2.3 Hz, C_6H_6), 119.6 (s, *m*-Mes*), 145.6 (s, *p*-Mes*), 145.7 (s, *o*-Mes*), 174.8 (dd, ^1J(P,C) = 105 Hz, ^3J(P,C) = 17.0 Hz, *i*-Mes*); ^{31}P{^{1}H} NMR (101.3 MHz, C_6D_6, 300 K): δ = 800.5 (d, ^2J(P,P) = 36.7 Hz, Ru=*P*), −14.0 (d, ^2J(P,P) = 36.7 Hz, Ru-*P*Me_3); HRMS: calcd for $C_{27}H_{44}P_2Ru$: 532.19611; found: 532.19541.

[(η^6-C_6H_6)(CO)Ru=PMes*] (12): In a fashion similar to that described for **9**, **8a** (160 mg, 0.20 mmol), DBU (59.8 μL, 0.40 mmol), and carbon monoxide (which was passed through the reaction mixture) were used to give a dark brown-green solution that contained small amounts of **12** (< 10 %) and intractable materials. ^{31}P NMR (101.3 MHz, C_6D_6, 300 K): δ = 896.6 (s, Ru=*P*).

[(η^6-C_6H_6)(*t*BuNC)Ru=PMes*] (13): In a fashion similar to that described for **3**, **8a** (106 mg, 0.20 mmol), DBU (59.8 μL, 0.40 mmol) and *t*BuNC (20.8 mg, 28.3 μL 0.25 mmol) were used to give dark brown-green crystals of **13** (90 mg, 0.167 mmol, 84 %). M.p. > 145 °C (decomp); ^{1}H NMR (250.13 MHz, C_6D_6, 300 K): δ = 1.21 (s, 9H, CN-C(CH_3)$_3$), 1.48 (s, 9H, *p*-C(CH_3)$_3$), 1.65 (s, 18H, *o*-C(CH_3)$_3$), 4.80 (s, 6H, C_6H_6), 7.47 (s, 2H, *m*-Mes*); ^{13}C{^{1}H} NMR (62.90 MHz, C_6D_6, 300 K): δ = 31.0 (s, C(*C*H$_3$)$_3$), 31.8 (s, C(*C*H$_3$)$_3$), 32.9 (d, ^4J(P,C) = 7.2 Hz, *o*-C(*C*H$_3$)$_3$), 34.9 (s, *p*-*C*(CH$_3$)$_3$), 38.6 (s, *o*-*C*(CH$_3$)$_3$), 56.2 (s, N*C*(CH$_3$)$_3$), 85.0 (s, C_6H_6), 119.6 (s, *m*-Mes*), 143.8 (s, *p*-Mes*), 145.8 (s, *o*-Mes*), 156.6 (br s, *C*N), 174.5 (d, ^1J(P,C) = 107.0 Hz, *i*-Mes*); ^{31}P NMR (101.3 MHz, C_6D_6, 300 K): δ = 821.1 (s, Ru=P); IR (KBr): $\tilde{\nu}$(CN) = 2101 cm^{-1}; HRMS: calcd for $C_{29}H_{44}NPRu$: 539.22546; found 539.22293.

Synthesis of 16: A red-brown solution of **8a** (106 mg, 0.20 mmol) in CH_2Cl_2 (2.5 mL) was added dropwise to a solution of DBU (59.8 μL, 0.40 mmol) in toluene (5 mL) at room temperature, and stirred for an additional 5 min. After removal of the solvents, the red-brown residue was extracted with *n*-pentane (15 mL), filtered, and concentrated to a few mL. Cooling at −20 °C yielded orange-red crystals of **16** (63 mg, 0.069 mmol, 69 %). ^{1}H NMR (400.13 MHz, C_6D_6, 340 K): δ = 1.37 (s, 18H, C(CH_3)$_3$), 1.59 (s, 6H, CH_3), 1.62 (s, 9H, C(CH_3)$_3$), 1.81 (s, 18H, C(CH_3)$_3$), 2.11 (dd, ^2J(P,H) = 4.1 Hz, ^4J(P,H) = 2.5 Hz, 2H, CH_2), 4.90 (s, 12H, C_6H_6), 5.29 (dd, ^1J(P,H) = 356 Hz, ^3J(P,H) = 30.3 Hz, 1H, P*H*), 7.21 (d, ^4J(H,H) = 1.9 Hz, 1H, Ar*H*), 7.38 (dd, ^4J(H,H) = 1.9 Hz, ^4J(P,H) = 3.7 Hz, 1H, Ar*H*), 7.44 (d, ^4J(P,H) = 1.8 Hz, 2H, *m*-Mes*); ^{13}C{^{1}H} NMR (100.64 MHz, C_6D_6, 340 K): δ = 31.2 (s, C(*C*H$_3$)$_3$), 31.4 (s, *C*H$_3$), 31.5 (s, C(*C*H$_3$)$_3$), 33.8 (d, ^4J(P,C) = 1.3 Hz, C(*C*H$_3$)$_3$), 34.7 (br s, C(*C*H$_3$)$_3$), 34.9 (d, ^3J(P,C) = 0.8 Hz, *C*(CH$_3$)$_3$), 35.0 (d,

^3J(P,C) = 0.8 Hz, $C(CH_3)_3$), 36.2 (dd, ^1J(P,C) = 19.5 Hz, ^3J(P,C) = 9.5 Hz, CH_2), 37.9 (s, $C(CH_3)_3$), 38.8 (s, $C(CH_3)_3$), 41.7 (d, ^2J(P,C) = 3.4 Hz, $C(CH_3)_2$), 82.2 (d, ^2J(P,C) = 1.5 Hz, C_6H_6), 118.0 (d, ^3J(P,C) = 7.3 Hz, *m*-Ar), 120.8 (d, ^3J(P,C) = 6.7 Hz, *m*-Ar), 120.9 (d, ^3J(P,C) = 7.6 Hz, *m*-Mes*), 144.1 (m, *i*-Ar), 144.3 (m, *i*-Mes*), 147.0 (d, ^4J(P,C) = 3.0 Hz, *p*-Mes*), 150.4 (d, ^2J(P,C) = 5.5 Hz, *o*-Ar), 151.0 (d, ^4J(P,C) = 2.4 Hz, *p*-Ar), 154.7 (br s, *o*-Mes*), 155.8 (d, ^2J(P,C) = 12.9 Hz, *o*-Ar); ^{31}P NMR (101.25 MHz, C_6D_6, 300 K): δ = 40.8 (dd, ^1J(P,H) = 356 Hz, ^2J(P,P) = 78.2 Hz, *P*H), 111.0 (dd, ^2J(P,P) = 78.2 Hz, ^3J(P,H) = 29.9 Hz, *P*Mes*); elemental analysis calcd (%) for $C_{48}H_{70}P_2Ru_2$: C 63.27, H 7.75, P 6.80; found: C 63.32, H 7.96,P 6.56.

Synthesis of 26: A red-brown solution of **8a** (106 mg, 0.20 mmol) in CH_2Cl_2 (2.5 mL) was added dropwise to a solution of DBU (59.8 μL, 0.40 mmol) and but-2-yne (1.0 mL, excess) in toluene (5 mL) at 0 °C, and stirred for an additional 5 min. After warming to room temperature, the solvents were removed and the residue was extracted with *n*-pentane (20 mL), filtered, and concentrated. Cooling at −20 °C yielded large air-sensitive orange-yellow crystals of **26** (78 mg, 0.153 mmol, 77 %). ^{1}H NMR (400.13 MHz, C_6D_6, 300 K): δ = 1.17 (s, 3H, CH_3), 1.26 (s, 3H, CH_3), 1.30 (s, 9H, $C(CH_3)_3$), 1.36 (br s, 2H, CH_2), 1.55 (d, ^3J(H,H) = 5.8 Hz, 3H, CH_3), 1.61 (d, ^3J(P,H) = 7.3 Hz, 3H, CH_3), 1.88 (m, 1H, C*H*), 1.89 (s, 9H, $C(CH_3)_3$), 5.12 (d, ^3J(P,H) = 0.6 Hz, 6H, C_6H_6), 7.23 (d, ^4J(H,H) = 1.8 Hz, 1H, C_6H_2), 7.59 (dd, ^4J(H,H) = 1.8 Hz, ^4J(P,H) = 4.8 Hz, 1H, C_6H_2); ^{13}C{^{1}H} NMR (100.64 MHz, C_6D_6, 300 K): δ = 16.0 (d, ^2J(P,C) = 3.0 Hz, CH_3), 21.1 (d, ^3J(P,C) = 16.0 Hz, CH_3), 28.2 (s, CH_3), 31.2 (d, ^3J(P,C) = 8.6 Hz, CH_3), 31.4 (s, $C(CH_3)_3$), 32.0 (d, ^2J(P,C) = 7.2 Hz, C=*C*H), 33.9 (d, ^4J(P,C) = 3.0 Hz, $C(CH_3)_3$), 34.8 (d, ^1J(P,C) = 13.8 Hz, CH_2), 35.1 (s, $C(CH_3)_3$), 37.9 (s, $C(CH_3)_3$), 41.5 (d, ^2J(P,C) = 6.6 Hz, $C(CH_3)_2$), 43.3 (d, ^1J(P,C) = 16.6 Hz, C=*C*-P), 80.3 (d, ^2J(P,C) = 1.7 Hz, C_6H_6), 118.1 (d, ^3J(P,C) = 7.7 Hz, *m*-C_6H_2), 122.1 (d, ^3J(P,C) = 8.1 Hz, *m*-C_6H_2), 153.2 (d, ^4J(P,C) = 2.2 Hz, *p*-PC_6H_2), 154.2 (d, ^2J(P,C) = 9.3 Hz, *o*-C_6H_2), 159.8 (d, ^2J(P,C) = 10.5 Hz, *o*-C_6H_2); ^{31}P{1H} NMR (101.25 MHz, C_6D_6, 300 K): δ = −4.42 (s).

Crystal structure determination of complexes 4, 9, and 26: X-ray intensities were collected on a Nonius KappaCCD diffractometer with rotating anode, using graphite-monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å). The structures were solved by automated Patterson methods (DIRDIF-97)[30] and refined with SHELXL-97[31] against F^2 of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters, hydrogen atoms were refined as rigid groups. The data of compound **4** were merged with SortAV[32] prior to the refinement. In structure **9**, the pentane solvent molecule was refined with a disorder model. Structure calculations and drawings were performed with the program PLATON.[33] Details of the structure determinations are given in Table 3.

Table 3. Crystallographic data for structures **4**, **9**, and **26**.

	4	**9**	**26**
formula	$C_{46}H_{58}OsP_2$	$C_{42}H_{50}P_2Ru \cdot C_5H_{12}$	$C_{28}H_{41}PRu$
F_w	863.06	789.98	509.65
crystal size [mm^3]	0.39 × 0.30 × 0.06	0.30 × 0.22 × 0.17	0.24 × 0.06 × 0.04
T [K]	110(2)	150(2)	125(2)
crystal system	orthorhombic	monoclinic	triclinic
space group	$Pca2_1$ (no. 29)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)
a [Å]	16.5396(2)	18.0784(2)	10.7621(2)
b [Å]	14.2128(1)	11.5440(1)	11.0806(2)
c [Å]	17.1697(2)	25.4258(3)	11.4412(3)
α [°]	90	90	72.1176(7)
β [°]	90	127.0777(7)	83.8048(8)
γ [°]	90	90	79.9689(15)
V [Å^3]	4036.15(7)	4233.45(9)	1276.45(5)
Z	4	4	2
ρ_{calcd} [g cm^{-3}]	1.420	1.239	1.326
μ [mm^{-1}]	3.269	0.476	0.689
abs. correction	analytical	none	multiscan
transm. range	0.33–0.82	–	0.84–0.98
measured/unique refl.	46104/9192	40753/9668	15849/4608
$(\sin\theta/\lambda)_{max}$ [Å^{-1}]	0.65	0.65	0.60
refined parameters	454	474	285
$R1$ (obs./all refl.)	0.0185/0.0257	0.0353/0.0571	0.0315/0.0509
$wR2$ (obs./all refl.)	0.0412/0.0464	0.0772/0.0839	0.0604/0.0665
S	0.604	1.031	0.919

CCDC-197637 (**4**), 197638 (**9**) and 197639 (**26**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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