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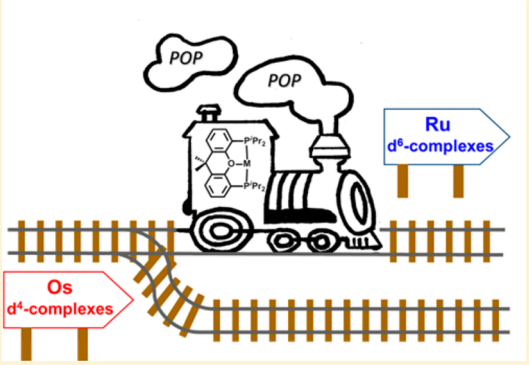
POP–Pincer Ruthenium Complexes: d^6 Counterparts of Osmium d^4 Species

Joaquín Alós, Tamara Bolaño, Miguel A. Esteruelas,* Montserrat Oliván, Enrique Oñate, and Marta Valencia

Departamento de Química Inorgánica, Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), Universidad de Zaragoza–CSIC, 50009 Zaragoza, Spain

Supporting Information

ABSTRACT: A wide range of ruthenium complexes stabilized by the POP–pincer ligand xant(P^iPr_2)$_2$ (9,9-dimethyl-4,5-bis(diisopropylphosphino)-xanthene) were prepared starting from *cis*-$RuCl_2\{\kappa$-*S*-$(DMSO)_4\}$ (**1**; DMSO = dimethyl sulfoxide). Treatment of toluene solutions of this adduct with the diphosphine under reflux leads to $RuCl_2\{xant(P^iPr_2)_2\}(\kappa$-*S*-DMSO) (**2**), which reacts with H_2 in the presence of a Brønsted base. The reaction in the presence of Et_3N affords $RuHCl\{xant(P^iPr_2)_2\}(\kappa$-*S*-DMSO) (**3**), whereas NaH removes both chloride ligands to give $RuH_2\{xant(P^iPr_2)_2\}(\kappa$-*S*-DMSO) (**4**). The stirring of **3** in 2-propanol under 3 atm of H_2 for a long time produces the elimination of DMSO and the coordination of H_2 to yield the dihydrogen derivative, $RuHCl(\eta^2$-$H_2)\{xant(P^iPr_2)_2\}$ (**5**). In contrast to H_2, PPh_3 easily displaces DMSO from the metal center of **3** to afford $RuHCl\{xant(P^iPr_2)_2\}(PPh_3)$ (**6**), which can be also obtained starting from $RuHCl(PPh_3)_3$ (**7**) and xant(P^iPr_2)$_2$. In contrast to **3**, complex **4** does not undergo DMSO elimination to give $RuH_2(\eta^2$-$H_2)\{xant(P^iPr_2)_2\}$ (**8**) under a H_2 atmosphere. However, the latter can be prepared by hydrogenation of Ru(COD)(COT) (**9**; COD = 1,5-cyclooctadiene and COT = 1,3,5-cyclooctatriene) in the presence of xant(P^iPr_2)$_2$. A more efficient procedure to obtain **8** involves the sequential hydrogenation with ammonia borane of the allenylidene derivative $RuCl_2(=C=C=CPh_2)\{xant(P^iPr_2)_2\}$ (**10**), which is formed from the reaction of **2** with 1,1-diphenyl-2-propyn-1-ol. The hydrogenation initially gives $RuCl_2(=C=CHCHPh_2)\{xant(P^iPr_2)_2\}$ (**11**), which undergoes the subsequent reduction of the Ru–C double bond to yield the hydride-tetrahydroborate complex, $RuH(\eta^2$-$H_2BH_2)\{xant(P^iPr_2)_2\}$ (**12**). The osmium complex, $OsCl_2\{xant(P^iPr_2)_2\}(\kappa$-*S*-DMSO) (**13**), reacts with 1,1-diphenyl-2-propyn-1-ol in a similar manner to its ruthenium counterpart **2** to yield the allenylidene derivative, $OsCl_2(=C=C=CPh_2)\{xant(P^iPr_2)_2\}$ (**14**). Ammonia borane also reduces the C_β–C_γ double bond of the allenylidene of **14**. However, the resulting vinylidene species, $OsCl_2(=C=CHCHPh_2)\{xant(P^iPr_2)_2\}$ (**15**), is inert. Complex **12** is an efficient catalyst precursor for the hydrogen transfer from 2-propanol to ketones, the α-alkylations of phenylacetonitrile and acetophenone with alcohols, and the regio- and stereoselective head-to-head (Z) dimerization of terminal alkynes.



INTRODUCTION

We are interested in complexes of platinum group metals with POP ligands such as 9,9-dimethyl-4,5-bis(diisopropylphosphino)-xanthene (xant(P^iPr_2)$_2$) and 4,6-bis(diisopropylphosphino)-dibenzofuran (dbf(P^iPr_2)$_2$) and in the study of the similarities and differences between the 4d and 5d counterparts of each group in the search for new, more efficient, and robust catalysts than those based on *trans*-$M(P^iPr_3)_2$ metal fragments.[1] Thus, we have recently shown access to the $Rh\{xant(P^iPr_2)_2\}$ and $Ir\{xant(P^iPr_2)_2\}$ chemistry and revealed marked differences in behavior between both metals,[2] which are the result of the higher reducing character and preference for saturated compounds of iridium.[2,3] For instance, the $Rh\{xant(P^iPr_2)_2\}$ metal fragment favors unsaturated d^8-square planar and d^6-five-coordinate silyl complexes, whereas the $Ir\{xant(P^iPr_2)_2\}$ metal fragment stabilizes saturated d^6-silyl derivatives. The stabilization of saturated d^6-$Rh\{xant(P^iPr_2)_2\}$ species seems to need the presence of a coordinated π-donor ligand such as chloride.[4]

The differences between osmium and ruthenium are particularly evident in the behavior of their hydride complexes toward alkynes and other unsaturated organic molecules.[5] The osmium-hydride complexes, with an stoichiometric chemistry much richer than that of ruthenium, facilitate carbon–carbon and carbon–heteroatom coupling reactions.[6] Some months ago, we showed the entry to $Os\{xant(P^iPr_2)_2\}$ hydride complexes. Some of them are hydrogen reservoirs, losing molecular hydrogen under mild conditions. An example is the hexahydride $OsH_6\{xant(P^iPr_2)_2\}$, which releases H_2 to afford $OsH_4\{xant-(P^iPr_2)_2\}$. This osmium(IV) tetrahydride is able to promote the reduction of H^+ and the head-to-head (Z) dimerization of

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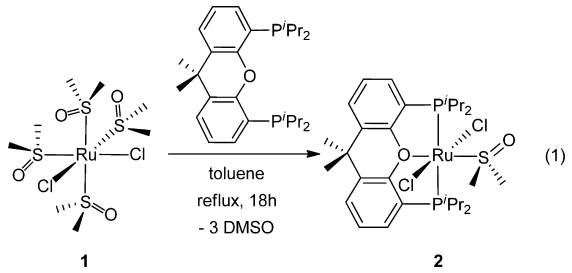
terminal alkynes to give (Z)-RC≡CCH=CHR enynes.[7] Now, we have investigated the chemistry of Ru{xant(P^iPr_2)$_2$} hydrides.

Ruthenium complexes with POP ligands are scarce in comparison with the plethora of reported compounds of this element with PNP,[8] PCP,[9] PNN,[10] and CNN[11] groups. The most studied systems are based on the xantphos ligand, which coordinates in a bidentate fashion in the vast majority of cases.[12] Although tridentate coordination has been proposed to have relevance in a number of catalytic processes,[13] few fully characterized examples with this coordination mode have been reported. Whittlesey described the cationic aqua cation [RuH(xantphos)(H_2O)(PPh_3)]$^+$ and studied its reactivity toward O_2, H_2, N_2, and amine-boranes.[14] James isolated and charaterized by X-ray diffraction analysis complexes containing organic fragments resulting from dehydrogenation of CH_2OH moieties in 3-hydroxy-2-(2-methoxyphenoxy)-1-phenyl-1-propanone and 2-(2-methoxyphenoxy)-1-phenyl-1,3-propanediol during the investigation of the hydrogenolysis mechanism of β-O-4 lignin model dimers.[15] Mol prepared and characterized by X-ray diffraction analysis the carbene derivative $RuCl_2$(=CHPh)(xantphos), which showed no activity in olefin metathesis reactions.[16] Karat has reported the synthesis and X-ray structure of $RuCl_2$(xantphos){κ-S-(DMSO)}, which shows a fac coordination of the tridentate ligand and is a modest catalyst precursor for the hydrogen transfer from 2-propanol to ketones in the presence of KOH.[17] Less used POP diphosphines include bis(2-(diphenylphosphino)phenyl)ether (DPEphos), $(R_2PCH_2CH_2)_2O$, and dbf(PPh_2)$_2$. Balakrisma synthesized complexes containing bidentate or tridentate, with fac or mer coordination, DPEphos ligands and studied their catalytic activities in the hydrogenation of styrene.[18] Gusev investigated the influence of the ^{i}Pr and ^{t}Bu substituents of $(R_2PCH_2CH_2)_2O$ on the behavior of Ru{$(R_2PCH_2CH_2)_2O$} complexes toward H_2 and O_2,[19] whereas Stephan described the synthesis of (alkylidene)-Ru{$(R_2PCH_2CH_2)_2O$} derivatives and provided examples of the direct interconversion between alkylidene and hydride-alkylidyne species.[20] Haenel reported $RuCl_2${dbf(PPh_2)$_2$}(PR_3) compounds with the diphosphine coordinated in a mer-tridentate fashion.[21]

This Article shows the entry to Ru{xant(P^iPr_2)$_2$} complexes; it reveals the similarities and differences between the chemistry of the latter and that of the osmium skeleton Os{xant(P^iPr_2)$_2$}, and it explores the ability of the hydride-tetrahydroborate complex RuH(η^2-H_2BH_2){xant(P^iPr_2)$_2$} as a catalyst precursor for the borrowing hydrogen methodology[22] and for the selective head-to-head (Z) dimerization of terminal alkynes.

RESULTS AND DISCUSSION

Entry to the Ru{xant(P^iPr_2)$_2$} Chemistry. An useful starting point for the development of the Os{xant(P^iPr_2)$_2$} chemistry has been the complex $OsCl_2${xant(P^iPr_2)$_2$}(κ-S-DMSO), which is prepared from the adduct *cis*-$OsCl_2${κ-S-(DMSO)$_4$} and xant(P^iPr_2)$_2$.[7] In light of this successful precedent, we started our work exploring a similar entry procedure for ruthenium (eq 1). Treatment of toluene solutions of *cis*-$RuCl_2${κ-S-(DMSO)$_4$} (**1**) with 1.0 equiv of the diphosphine under reflux, for 18 h, affords $RuCl_2${xant(P^iPr_2)$_2$}(κ-S-DMSO) (**2**), which was isolated as a yellow solid in 75% yield.



Complex **2** was characterized by X-ray diffraction analysis. Figure 1 shows a drawing of the molecule. In agreement with

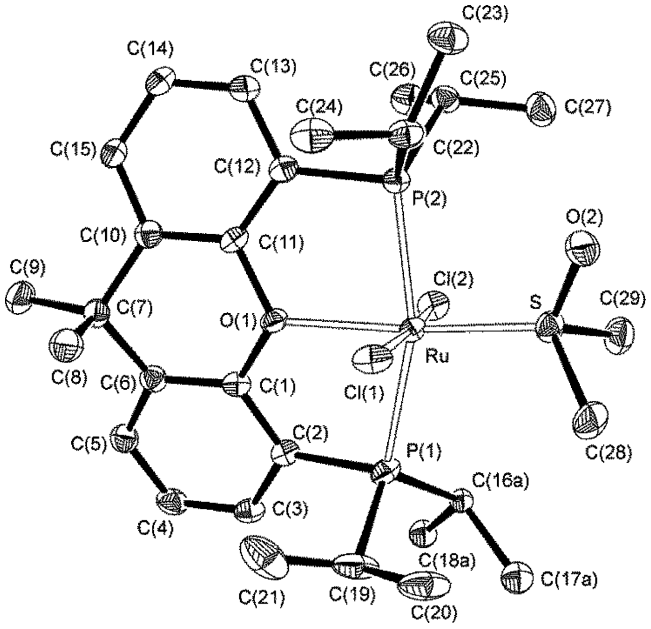


Figure 1. ORTEP diagram of complex **2** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru−S = 2.1775(7), Ru−O(1) = 2.2214(18), Ru−P(1) = 2.3870(7), Ru−P(2) = 2.3425(7), S−O(2) = 1.486(2), P(1)−Ru−P(2) = 161.74(3), P(1)−Ru−O(1) = 80.46(5), P(2)−Ru−O(1) = 81.84(5), Cl(1)−Ru−Cl(2) = 173.96(3), and O(1)−Ru−S = 172.98(5).

the osmium analogue but in contrast with the Ru(xantphos) counterpart,[17] the Ru{xant(P^iPr_2)$_2$} skeleton displays a mer coordination with P(1)−Ru−P(2), P(1)−Ru−O(1), and P(2)−Ru−O(1) angles of 161.74(3)°, 80.46(5)°, and 81.84(5)°, respectively. Thus, the coordination geometry around the metal center can be rationalized as a distorted octahedron with trans chloride ligands (Cl(1)−Ru−Cl(2) = 173.96(3)°) and the oxygen atom of the phosphine trans disposed to the dimethyl sulfoxide group, which is S-coordinated, as expected for the soft character of ruthenium (O(1)−Ru−S = 172.98(5)°). In accordance with the S bonding,[23] the IR spectrum shows the ν(S=O) band at 1090 cm^{-1}, which is consistent with a S−O(2) bond length of 1.486(2) Å. The mutual trans disposition of the chloride ligands is also evident in the ^{1}H and the ^{13}C{^{1}H} NMR spectra in dichloromethane-d_2 at room temperature, which contain two signals assigned to the methyl groups of the isopropyl substituents of the phosphine (δ_{1H}, 1.37 and 1.32; δ_{13C}, 21.8 and 20.9) and a signal for the methyl substituents of the central heterocycle (δ_{1H}, 1.63; δ_{13C}, 31.7). As expected for equivalent P^iPr_2 groups, the ^{31}P{^{1}H} NMR spectrum shows a singlet at 37.2 ppm.

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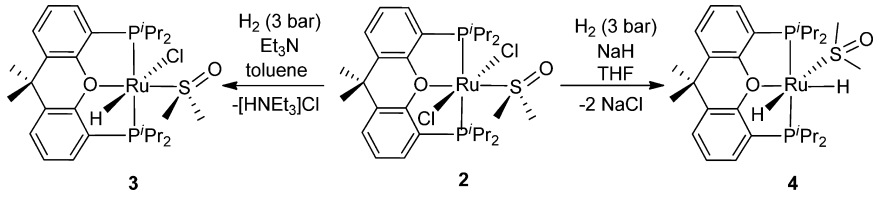
Scheme 1



Complex **2** reacts with molecular hydrogen in the presence of a Brønsted base. The reactions are very sensitive to the base used and the experimental conditions (Scheme 1). The stirring of toluene solutions of **2** with 2.1 equiv of Et_3N under 3 atm of hydrogen at 90 °C for 60 h produces the replacement of a chloride ligand by hydride to give the monohydride, RuHCl-{xant(P^iPr_2)$_2$}(κ-*S*-DMSO) (**3**), which was isolated as a pale yellow solid in 81% yield. In contrast to Et_3N in toluene, NaH in tetrahydrofuran causes the substitution of both chloride ligands. Thus, the treatment of tetrahydrofuran solutions of **2** with 10 equiv of the superbase under 3 atm of hydrogen at 50 °C for 90 h leads to *cis*-dihydride RuH_2{xant(P^iPr_2)$_2$}(κ-*S*-DMSO) (**4**), which was also isolated as a pale yellow solid but in 55% yield.

The osmium complex $OsCl_2${xant(P^iPr_2)$_2$}(κ-*S*-DMSO) also reacts with H_2 in the presence of a Brønsted base.[7] As for **2**, the reaction products depend upon the base and the experimental conditions: Et_3N in toluene produces the abstraction of a chloride ligand, whereas NaH in tetrahydrofuran causes the abstraction of both chloride ligands. Furthermore, in the case of osmium, H_2 displaces the dimethyl sulfoxide ligand. Thus, trihydride OsH_3Cl{xant(P^iPr_2)$_2$} is formed in the presence of Et_3N, whereas tetrahydride OsH_4{xant(P^iPr_2)$_2$}, via the hexahydride OsH_6{xant(P^iPr_2)$_2$}, is obtained when NaH is used (i.e., osmium reaches the oxidation states four and six, whereas ruthenium retains the oxidation state two).

Figure 2 shows a view of the molecule of **3**. As expected for a mer coordination of the diphosphine, the Ru{xant(P^iPr_2)$_2$} skeleton is T-shaped with the ruthenium atom situated in the common vertex and P(1)−Ru−P(2), P(1)−Ru−O(1), and P(2)−Ru−O(1) angles of 157.69(4)°, 80.21(7)°, and 80.64(7)°, respectively. Thus, the coordination geometry around the metal center can be rationalized as a distorted octahedron with the hydride and chloride ligands trans disposed (Cl−Ru−H(01) = 173.9(15)°), whereas the dimethyl sulfoxide molecule lies trans to the oxygen atom of the diphosphine (S−Ru−O(1) = 177.93(8)°). In agreement with its S coordination, the IR spectrum shows the ν(S═O) band at 1075 cm^{-1} along with the ν(Ru−H) vibration at 2019 cm^{-1}. The ^1H NMR spectrum in benzene-d_6 is also consistent with the presence of a hydride ligand in the complex. Thus, it contains a triplet with a H−P coupling constant of 21.7 Hz at −16.53 ppm. A singlet at 54.9 ppm in the $^{31}P\{^1H\}$ NMR spectrum is also characteristic of this compound.

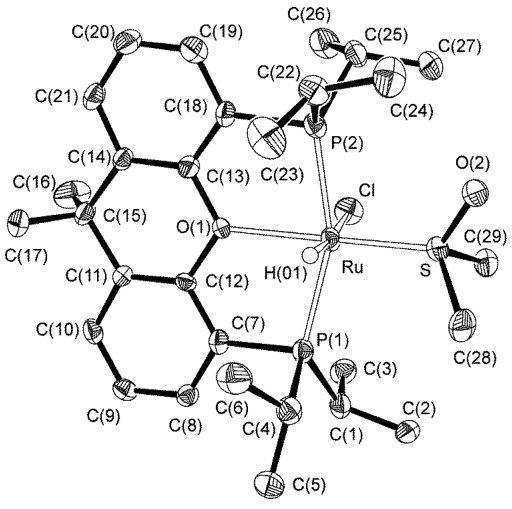


Figure 2. ORTEP diagram of complex **3** (50% probability ellipsoids). Hydrogen atoms (except hydride) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru−S = 2.1619(12), Ru−O(1) = 2.259(3), Ru−P(1) = 2.3351(13), Ru−P(2) = 2.3178(13), Ru−Cl = 2.5265(12), S−O(2) = 1.475(3), P(1)−Ru−P(2) = 157.69(4), P(1)−Ru−O(1) = 80.21(7), P(2)−Ru−O(1) 80.64(7), Cl−Ru−H(01) = 173.9(15), and S−Ru−O(1) = 177.93(8).

Complex **4** was also characterized by X-ray diffraction analysis. Figure 3 shows a drawing of the molecule. As with **2** and **3**, the Ru{xant(P^iPr_2)$_2$} skeleton is T-shaped with the metal situated in the common vertex. In this case, the bite angles P(1)−Ru−P(2), P(1)−Ru−O(1), and P(2)−Ru−O(1) are 149.68(3)°, 80.87(7)°, and 82.83(6)°, respectively. As expected for their strong trans influence,[24] the hydride ligands are cis disposed, with H(01)−Ru−S(1) and H(02)−Ru−O(1) angles of 172.8(12)° and 167.4(15)°, respectively, in a distorted octahedral geometry. The cis disposition of the hydride ligands is also supported by the IR spectrum, which contains two ν(Ru−H) bands at 1928 and 1898 cm^{-1}. According to the S coordination of the dimethyl sulfoxide molecule, the ν(S═O) vibration appears at 1091 cm^{-1}, in agreement with **2** and **3**.

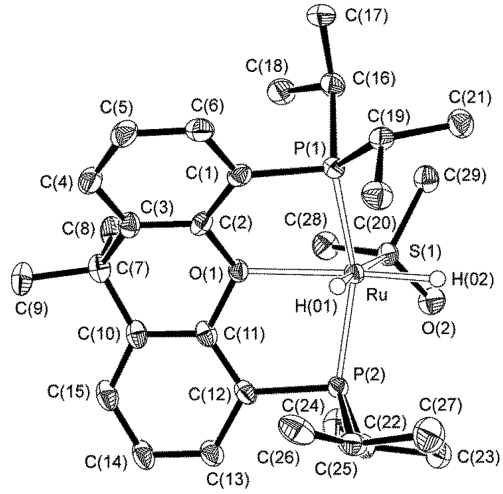


Figure 3. ORTEP diagram of complex **4** (50% probability ellipsoids). Hydrogen atoms (except hydrides) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru−S(1) = 2.2520(9), Ru−O(1) = 2.299(2), Ru−P(1) = 2.2767(9), Ru−P(2) = 2.2643(9), S(1)−O(2) = 1.491(3), P(1)−Ru−P(2) = 149.68(3), P(1)−Ru-O(1) = 80.87(7), P(2)−Ru−O(1) = 82.83(6), H(01)−Ru−S(1) = 172.8(12), and H(02)−Ru−O(1) = 167.4(15).

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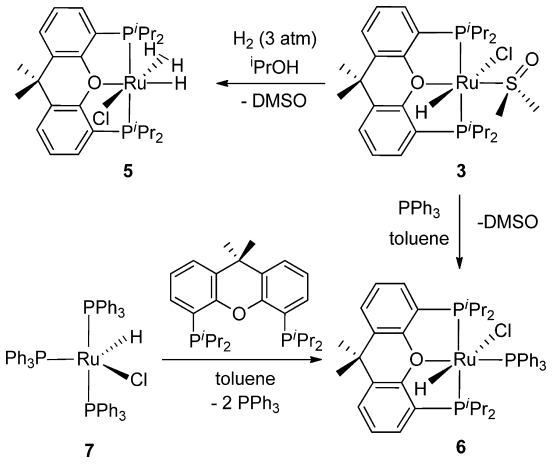
The ^{1}H NMR spectrum in benzene-d_6 is consistent with the IR and Figure 3. Thus, it shows two hydride resonances at −10.62 and −20.70 ppm, which are observed as double triplets with a H−H coupling constant of 7.5 Hz and H−P coupling constants of 30.2 and 18.6 Hz, respectively. The equivalent P^iPr_2 groups display a singlet at 74.4 ppm in the $^{31}P\{^1H\}$ NMR spectrum.

$RuHCl(\eta^2\text{-}H_2)\{xant(P^iPr_2)_2\}$ and $RuH_2(\eta^2\text{-}H_2)\{xant\text{-}(P^iPr_2)_2\}$. The stirring of **3** in 2-propanol under 3 atm of H_2 at 110 °C for a long time (4 weeks) produces the elimination of dimethyl sulfoxide and the coordination of a hydrogen molecule to the metal center. Thus, the reaction affords $RuHCl(\eta^2\text{-}H_2)\{xant(P^iPr_2)_2\}$ (**5**, Scheme 2), the ruthenium counterpart of $OsH_3Cl\{xant(P^iPr_2)_2\}$, which is, however, a hydride-dihydrogen derivative, in agreement with the tendency of ruthenium to avoid the oxidation state four. Because the osmium valence orbitals have better overlap with the ligand orbitals than ruthenium,[25] the latter is a poorer π-back-bonder, which favors nonclassical hydrogen−hydrogen interactions.[26]

Scheme 2



Complex **5** was isolated as a pale beige solid in 51% yield. The presence of three hydrogen atoms bonded to the metal center is strongly supported by its ^{1}H NMR spectrum in toluene-d_8, which shows a triplet (J_{H-P} = 13.2 Hz) at −12.28 ppm. This signal, which does not decoalesce between 293 and 183 K, exhibits a 400 MHz $t_{1(min)}$ value of 56 ± 3 ms at 243 K. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 72.1 ppm, supporting a mer coordination of the diphosphine.

Complex **5** undergoes H/D exchange at the RuH-positions with methanol-d_4. The observed NMR H−D coupling constant has a value of 6.2 Hz, which is an average owing to the exchange process in the hydride-dihydrogen unit. Assuming that the hydride-dihydrogen H−D coupling constants are all between 0 and 1 Hz,[27] the H−D coupling constant in the elongated dihydrogen ligand is between 16.6 and 18.6 Hz.[28] According to the standard Morris's empirical equation,[29] the calculated H−D coupling constant yields a H−H separation of about 1.1 Å.

DFT calculations (M06-LANL2DZ/6-31G**) reveal that there are three isomers with the chloride ligand cis-disposed to the oxygen atom of the diphosphine and the hydrogen atoms bonded to the metal center lying in the perpendicular plane to the P−Ru−P direction, which differ by 1.6 kcal mol^{-1} (ΔG, 1 atm, 298.15 K): the *trans*−Cl−Ru−H_2 derivatives **5a** and **5b** and the *trans*−O−Ru−H_2 species **5c**. Figure 4 shows views of the DFT-optimized structures. The main difference between **5a** and **5b** is the separation between the atoms of the coordinated hydrogen molecule: 1.248 Å for the first of them and 0.907 Å for the second one. The separation in **5c** of 0.933 Å is similar to that of **5b**. As expected, the average distance between the atoms of the dihydrogen ligand of 1.03 Å is consistent with that calculated from J_{H-D} and suggests a fast equilibrium between the three isomers in solution. The trans disposition of the

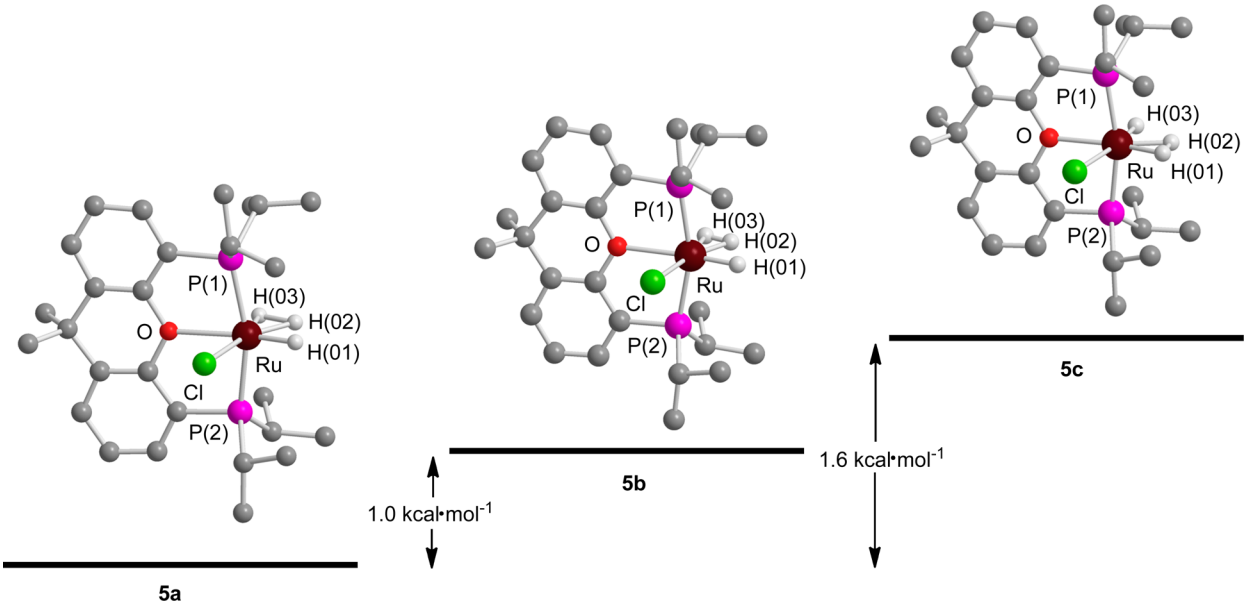


Figure 4. DFT-optimized structures of **5a**−**c**. Hydrogen atoms (except hydrides) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru−O = 2.305 (**5a**), 2.325 (**5b**), and 2.231 (**5c**); Ru−P(1) = 2.323 (**5a**), 2.325 (**5b**), and 2.315 (**5c**); Ru−P(2) = 2.323 (**5a**), 2.324 (**5b**), and 2.315 (**5c**); Ru−Cl = 2.508 (**5a**), 2.471 (**5b**), and 2.578 (**5c**); H(01)−H(02) = 1.649 (**5a**), 1.857 (**5b**), and 0.933 (**5c**); H(02)−H(03) = 1.248 (**5a**), 0.907 (**5b**), and 1.866 (**5c**); P(1)−Ru−P(2) = 163.5 (**5a**), 162.6 (**5b**), and 165.4 (**5c**); P(1)−Ru−O = 81.8 (**5a**), 81.5 (**5b**), and 82.7 (**5c**); P(2)−Ru−O = 81.8 (**5a**), 81.5 (**5b**), and 82.7 (**5c**); O−Ru−H(01) = 166.7 (**5a**), 171.5 (**5b**), and 166.7 (**5c**); and Cl−Ru−H(03) = 163.7 (**5a**), 167.7 (**5b**), and 170.0 (**5c**).

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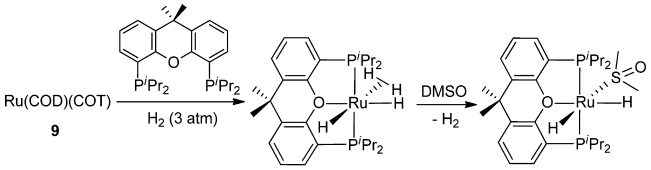
π-donor oxygen and chloride atoms causes the destabilization of **5**. Thus, there are also three *trans*−Cl−Ru−O dihydrogen structures (0.812−0.820 Å), which lie between 8.6 and 11.0 kcal mol^{-1} above **5a** (see the Supporting Information).

Triphenylphosphine, in contrast to molecular hydrogen, easily displaces dimethyl sulfoxide from the metal center of **3**. Thus, the treatment of toluene solutions of the latter with 1.2 equiv of the Lewis base at 80 °C for 1 h leads to RuHCl{xant(P^{i}Pr$_2$)$_2$}(PPh$_3$) (**6**), which was isolated as a yellow solid in 48% yield. This complex can be also obtained in 83% yield starting from the known Wilkinson's compound RuHCl(PPh$_3$)$_3$ (**7**)[30] and xant(P^{i}Pr$_2$)$_2$. The proposed structure for **6** in Scheme 2 is strongly supported by the ^{1}H and ^{31}P{^{1}H} NMR spectra of the obtained solids in dichloromethane-d_2 at room temperature. In agreement with the presence of the hydride ligand, the ^{1}H NMR spectrum shows a high-field resonance at −17.48 ppm, which compares well with that of **3** and is observed as a double triplet with typical cis H−P coupling constants of 27.9 and 24.0 Hz, whereas the ^{31}P{^{1}H} NMR spectrum contains a triplet at 76.4 ppm (PPh$_3$) and a doublet at 51.8 ppm (P^{i}Pr$_2$) that also display a typical cis P−P coupling constant of 31.2 Hz.

The formation of **5** according to Scheme 2 prompted us to explore a similar procedure to prepare a related RuH$_2$(η^2-H$_2$)-{xant(P^{i}Pr$_2$)$_2$} (**8**) species, the ruthenium counterpart of the osmium tetrahydride OsH$_4${xant(P^{i}Pr$_2$)$_2$}. However, all attempts were unsuccessful. So, following the procedure introduced by Chaudret in 1984 for the preparation of RuH$_2$(η^2-H$_2$)$_2$(PR$_3$)$_2$ derivatives,[31] we performed the hydrogenation of complex Ru(COD)(COT) (**9**, in Scheme 3;

Scheme 3



COD = 1,5-cyclooctadiene and COT = 1,3,5-cyclooctatriene) in the presence of 1.0 equiv of {xant(P^{i}Pr$_2$)$_2$} in pentane at room temperature under 3 atm of hydrogen for 24 h. This pathway allowed us to isolate **8** (Scheme 3) in about 40% yield as a pale yellow solid. The moderate efficiency of the method is a consequence of the high tendency of the starting complex to give ruthenium nanoparticles[32] under the reaction conditions, which gives rise to a decrease of the efficient ruthenium material in the reaction medium. We note that Leitner, Milstein, and co-workers synthesized, also in moderated yield, the RuH$_2$(η^2-H$_2$)(PNP) (PNP = 2,5-bis(di-*tert*-butylphosphanyl)lutidine) complex by hydrogenation of Ru(η^3-allyl)$_2$(COD) in the presence of the pincer diphosphine under 7 atm of hydrogen for 66 h.[33] However, under our milder conditions, the use of this starting complex was not successful (neither was the method of Belderrain and Grubbs successful, which involves the hydrogenation of [RuCl$_2$(COD)]$_x$ in the presence of the phosphine and an excess of NaOH in *sec*-butyl alcohol under 2 atm of hydrogen).[34]

Complex **8** is moderately stable in a solution of non-coordinating hydrocarbons as well as in the solid state under a hydrogen atmosphere. The addition of coordinating solvents to its solutions produces the displacement of the hydrogen molecule by the added solvent. Thus, the addition of dimethyl sulfoxide affords **4**. The most noticeable spectroscopic feature of **8** is a high-field resonance in the ^{1}H NMR spectrum in toluene-d_8, which appears at −9.18 ppm as a triplet with a H−P coupling constant of 14.0 Hz at room temperature and exhibits a 400 MHz $t_{1(\min)}$ value of 44 ± 3 ms at 233 K. This complex rapidly exchanges hydrogen by deuterium at the RuH positions even with deuterated hydrocarbon solvents. The observed NMR H−D coupling constant of 4.5 Hz is consistent with a H−D coupling constant in the dihydrogen ligand of between 26.0 and 27.0 Hz,[35] which corresponds to a hydrogen−hydrogen separation of about 0.9 Å. A singlet at 92.1 ppm in the ^{31}P{^{1}H} NMR spectrum is also characteristic of this dihydrogen complex.

Figure 5 shows the DFT-optimized structure of **8**, which is consistent with the minimum-energy structure of the

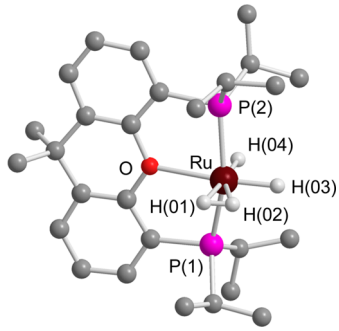


Figure 5. DFT-optimized structure of **8**. Hydrogen atoms (except hydrides) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru−O = 2.331, Ru−P(1) = 2.294, Ru−P(2) = 2.294, H(01)−H(02) = 0.849, H(03)−H(04) = 2.155, P(1)−Ru−P(2) = 158.1, P(1)−Ru−O = 81.1, P(2)−Ru−O(1) 81.1, O−Ru−H(03) = 168.7, and O−Ru−H(04) = 85.3.

RuH$_4$(PNP) complex.[36] The results suggest that the trans disposition of the coordinated hydrogen molecule to one of the hydride ligands is favored with regard to the π-donor oxygen atom of the diphosphine. Thus, the coordination polyhedron around the ruthenium can be described as a trans-hydride−dihydrogen octahedron with the diphosphine mer coordinated. The hydrogen molecule lies at the same plane as the oxygen atom of the diphosphine and the hydride ligands, perpendicularly disposed to the P−Ru−P direction. The separation between the hydrogen atoms of the dihydrogen ligand of 0.849 Å compares well with that calculated from the NMR H−D coupling constant.

Preparation of 8 via Allenylidene, Vinylidene, and Tetrahydroborate Intermediates. An efficient method to prepare polyhydride derivatives, in particular those of group 8 and 9 metals, involves the decomposition of tetrahydroborate derivatives in the presence of an alcohol. The latter are prepared from chloro complexes by means of the displacement of a chloride ligand by the tetrahydroborate group.[37] Attempts to prepare **8** by a similar procedure starting from **2** or **3** were unsuccessful. Both complexes react with NaBH$_4$ in the presence of methanol to give **4**. In view of that the problem seemed to be the dimethyl sulfoxide molecule of the starting compounds, we decided to substitute it by a better donor ligand, which should be at the same time a better leaving group. Then, we brought in an unsaturated hydrocarbon fragment, which could be reduced by action of ammonia borane. The hydrogen transfers from the

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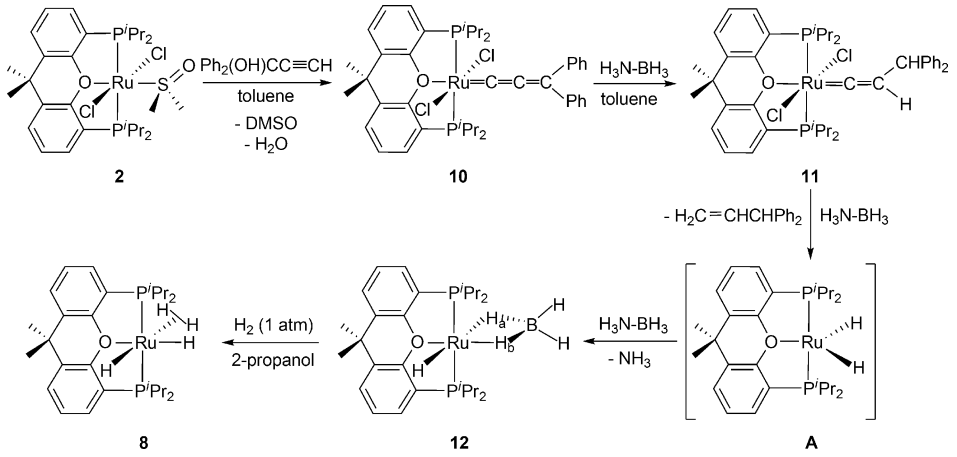
Scheme 4



latter to both C−C and C−heteroatom double bonds, in the presence and in the absence of a transition metal, are well-known processes.[38] As a source of the hydrocarbon fragment, we selected 1,1-diphenyl-2-propyn-1-ol, which can tautomerize and dehydrate to afford a diphenylallenylidene ligand.[39]

Treatment of toluene solutions of **2** with 3.0 equiv of the alkynol under reflux overnight leads to the allenylidene derivative, $RuCl_2(=C=C=CPh_2)\{xant(P^iPr_2)_2\}$ (**10**), which was isolated as a purple solid in 92% yield, according to Scheme 4.

Complex **10** was characterized by X-ray diffraction analysis. The structure has two chemically equivalent but crystallographically independent molecules in the asymmetric unit. Figure 6 shows a drawing of one of them. In agreement with **2**, the $Ru\{xant(P^iPr_2)_2\}$ skeleton displays a mer coordination with P(1)−Ru(1)−P(2), P(1)−Ru(1)−O(1), and P(2)−Ru(1)−O(1) angles of 164.03(7)° and 164.53(6)°, 81.53(12)° and 82.30(12)°, and 82.52(12)° and 82.23(12)°, respectively. Thus, the coordination polyhedron around the ruthenium atom can be rationalized as a distorted octahedron with trans chloride ligands (Cl(1)−Ru(1)−Cl(2) = 166.55(6)° and 165.06(6)°) and the allenylidene fragment trans disposed to the oxygen atom of the diphosphine (C(1)−Ru(1)−O(1) = 174.8(2)° and 177.3(2)°). The hydrocarbon is bonded to the metal in a nearly linear fashion, with Ru(1)−C(1)−C(2) and C(1)−C(2)−C(3) angles of 176.0(6)° and 175.5(6)° and 169.6(7)° and 170.6(7)°, respectively. The Ru(1)−C(1), C(1)−C(2), and C(2)−C(3) bond lengths of 1.824(7) (both molecules), 1.272(9) and 1.271(9), and 1.357(9) and 1.353(9) Å, respectively, compare well with those reported for other ruthenium-allenylidene complexes.[40] In this context, it should be noted that C(1)−C(2) and C(2)−C(3) are shorter and longer, respectively, than the bond length expected for a C−C double bond (about 1.30 Å), indicating a substantial contribution of the canonical form $M^+-C\equiv C-\bar{C}Ph_2$ to the structure of **10**. The presence of an allenylidene ligand in the complex is also supported by the IR spectrum, which shows the characteristic $\nu(C=C=C)$ band of this type of ligands at 1889 cm^{-1}. In the $^{13}C\{^1H\}$ NMR spectrum in benzene-d_6, this ligand displays two singlets at 147.3 and 253.5 ppm and a triplet (J_{C-P} = 12.8 Hz) at 308.8 ppm, which are assigned to the C_γ (C(3)), C_β (C(2)), and C_α (C(1)) atoms, respectively, on the basis of the HMBC spectrum. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 46.9 ppm, as expected for equivalent P^iPr_2 groups.

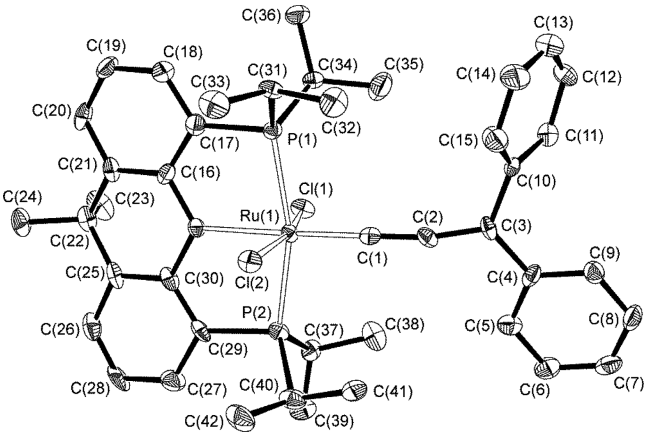


Figure 6. ORTEP diagram of one of the two crystallographically independent molecules of complex **10** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru(1)−Cl(1) = 2.3925(17), 2.3918(17), Ru(1)−Cl(2) = 2.3729(17), 2.3654(17), Ru(1)−O(1) = 2.232(4), 2.225(4), Ru(1)−P(1) = 2.3555(18), 2.3432(19), Ru(1)−P(2) = 2.3321(19), 2.3353(18), Ru(1)−C(1) = 1.824(7), 1.824(7), C(1)−C(2) = 1.272(9), 1.271(9), C(2)−C(3) = 1.357(9), 1.353(9), P(1)−Ru(1)−P(2) = 164.03(7), 164.53(6), P(1)−Ru(1)−O(1) = 81.53(12), 82.30(12), P(2)−Ru(1)−O(1) = 82.52(12), 82.23(12), Cl(1)−Ru(1)−Cl(2) = 166.55(6), 165.06(6), C(1)−Ru(1)−O(1) = 174.8(2), 177.3(2), Ru(1)−C(1)−C(2) = 176.0(6), 175.5(6), and C(1)−C(2)−C(3) = 169.6(7), 170.6(7).

Ammonia borane reduces the allenylidene ligand. The reduction is sequential, although its selectivity is low (Figure 7). Treatment of toluene solutions of **10** with 12.0 equiv of ammonia borane at room temperature produces the initial hydrogenation of the $C_\beta-C_\gamma$ double bond to form the vinylidene complex, $RuCl_2(=C=CHCHPh_2)\{xant(P^iPr_2)_2\}$ (**11**), which undergoes the subsequent hydrogenation of the Ru−C_α double bond to give the hydride-tetrahydroborate complex, $RuH(\eta^2\text{-}H_2BH_2)\{xant(P^iPr_2)_2\}$ (**12**) and 3,3-diphenyl-1-propene, detected by GC−MS. The formation of **12** could take place via the unsaturated dihydride $RuH_2\{xant(P^iPr_2)_2\}$ (**A**) resulting from the substitution of the chloride ligands by hydrides. Thus, the reaction of this dihydride with the excess of ammonia borane should give **12**. There are precedents for this process: Heinekey and Goldberg have reported that the iridium-dihydride $IrH_2(POCOP)$ (POCOP = η^3-1,3-$(OP^tBu_2)_2C_6H_3$) reacts with an excess of BH_3·THF to afford $IrH(\eta^2\text{-}H_2BH_2)(POCOP)$.[41]

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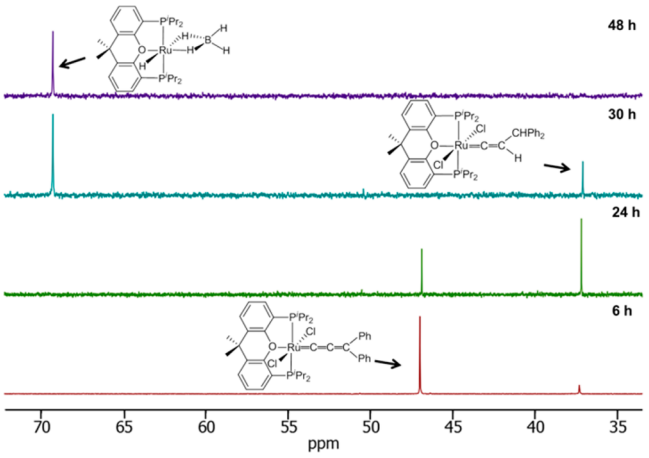


Figure 7. Stacked $^{31}P\{^1H\}$ NMR spectra showing the transformation of allenylidene complex **10** into hydride-tetrahydroborate derivative **12** via vinylidene **11**.

The hydrogenation of allenylidene compounds has received scarce attention. We have reported the selective ionic reduction of the $C_\alpha-C_\beta$ double bond of the allenylidene ligand of the complex $[OsH(=C=C=CPh_2)(CH_3CN)_2(P^iPr_3)_2]BF_4$ by hydrogen transfer from alcohols. The hydrogenation leads to the hydride carbene $[OsH(=CHCH=CPh_2)(CH_3CN)_2(P^iPr_3)_2]BF_4$, which subsequently undergoes the intramolecular reduction of the $Os-C_\alpha$ double bond to give 1,1-diphenylpropene and $[Os\{CH_2CH(CH_3)P^iPr_2\}(CH_3CN)_3(P^iPr_3)]BF_4$.[24] Furthermore, we have described the formation of vinylidene $Os(\eta^5\text{-}C_5H_5)Cl(=C=CHCHPh_2)(P^iPr_3)$ by reduction of the $C_\beta\text{-}C_\gamma$ double bond of the allenylidene ligand of $Os(\eta^5\text{-}C_5H_5)Cl(=C=C=CPh_2)(P^iPr_3)$ with $NaBH_4$ and some drops of methanol.[42] In the same line, Che, Phillips, and co-workers observed that the treatment of *trans*-$[Cl(16\text{-}TMC)Ru(=C=C=CPh_2)]PF_6$ complex with Zn/Hg in methanol under reflux leads to *trans*-$[Cl(16\text{-}TMC)Ru(=C=CHCHPh_2)]PF_6$ (16-TMC = 1,5,9,13-tetramethyl-1,5,9,13-tetraazacyclohexadecane).[43] Werner and co-workers reported the hydrogenation of the $M-C_\alpha$ double bond of $MCl\{=C=C=C(R)Ph\}(P^iPr_3)_2$ with molecular hydrogen to give allene compounds $MCl\{\eta^2\text{-}CH_2=C=C(R)Ph\}(P^iPr_3)_2$ (M = Rh,[44] Ir[45]).

Complex **11** was fully characterized by ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy. The most noticeable resonances in the ^1H NMR spectrum in benzene-d_6 are a doublet (J_{H-H} = 10.5 Hz) at 5.60 ppm and a double triplet (J_{H-H} = 10.5; J_{H-P} = 3.0 Hz) at 4.68 ppm because of the HC(sp^2) and HC(sp^3) hydrogen atoms of the vinylidene ligand, respectively. In the $^{13}C\{^1H\}$ NMR spectrum, the vinylidene C(sp^2) resonances appear at 346.4 (C_α) and 106.9 (C_β) ppm as triplets with C–P coupling constants of 12.8 and 3.0 Hz, respectively, whereas the C(sp^3) signal is observed at 41.7 ppm as a singlet. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 37.3 ppm, supporting the mer coordination of the diphosphine.

Complex **12** was isolated as a yellow solid in 75% yield with regard to **10**. In support of the structure proposed in Scheme 4, the ^1H NMR spectrum in toluene-d_8 at 243 K shows two unresolved resonances at −4.77 (H_a) and −23.92 (H_b) ppm, assigned to the bridging Ru–H–B hydrogen atoms, whereas the hydride ligand displays at −15.35 ppm a double triplet with $H-H_b$ and H–P coupling constants of 8.0 and 20.0 Hz, respectively. In the low-field region of the spectrum, the terminal BH_2 hydrogen atoms give rise to a broad resonance centered at about 6.1 ppm. In solution, the structure is rigid at temperatures lower than 243 K. Between the latter and 293 K, exchange processes take place that involve the bridging hydrogen atoms and the terminal hydrogen attached to boron but not the hydride ligand. In agreement with this, between 243 and 293 K, the resonance at 6.1 ppm disappears in the baseline, whereas the bridging Ru–H–B resonances broaden. A similar behavior has been reported for complexes $MH(\eta^2\text{-}H_2BH_2)(CO)(P^iPr_3)_2$ (M = Ru, Os)[37d] and $RuH(\eta^2\text{-}H_2BH_2)(^t$BuPNN) (^{t}BuPNN = 2-di-*tert*-butylphosphino-methyl-6-diethylaminomethylpyridine).[8e] According to the mer coordination of the diphosphine, the $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 69.5 ppm. A broad signal at 31.7 ppm in the $^{11}B\{^1H\}$ NMR spectrum is also characteristic of this compound.

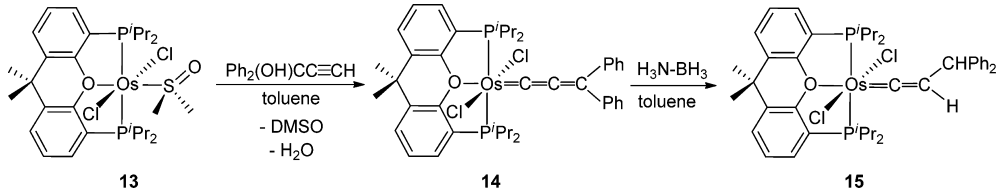
Complex **12** is stable in a solution of hydrocarbons and in the solid state at room temperature under argon. However, its stirring in 2-propanol under 1 atm of hydrogen at 80 °C for 24 h gives rise to the formation of **8** in quantitative yield (Scheme 4).

Hydrogenation of the Allenylidene Ligand of an Osmium Counterpart of 10. In view of the results summarized in Scheme 4, some questions arise: What happens with osmium? Is it possible to apply the same methodology to prepare the osmium counterpart of **8**, the tetrahydride derivative $OsH_4\{xant(P^iPr_2)_2\}$? Does the metal element in the hydrogenation of the allenylidene ligand have any influence?

Complex $OsCl_2\{xant(P^iPr_2)_2\}(\kappa\text{-}S\text{-}DMSO)$ (**13**) reacts with 1,1-diphenyl-2-propyn-1-ol in the same manner as its ruthenium analogue, **2**. Treatment of toluene solutions of **13** with 3.0 equiv of the alkynol under reflux overnight leads to the osmium-allenylidene derivative $OsCl_2(=C=C=CPh_2)\{xant(P^iPr_2)_2\}$ (**14**) as consequence of the substitution of the dimethyl sulfoxide molecule by the alkynol and the subsequent tautomerization and dehydration of the latter (Scheme 5).

Complex **14** was isolated as a yellow solid in 82% yield and was characterized by X-ray diffraction analysis. Figure 8 shows a view of its structure. As for **10**, the coordination polyhedron around the metal center can be described as a distorted octahedron with the diphosphine mer-coordinated (P(1)–Os–P(2) = 162.98(4)°, P(1)–Os–O(1) = 81.45(8)°, and P(2)–Os–O(1) = 81.76(8)°) and the allene trans disposed to the oxygen atom of the diphosphine (C(1)–Os–O(1) = 179.07(16)°, Cl(1)–Os–Cl(2) = 165.38(4)°). The hydrocarbon fragment is bonded to the osmium atom in a nearly linear fashion, with Os–C(1)–C(2) and C(1)–C(2)–C(3) angles of

Scheme 5



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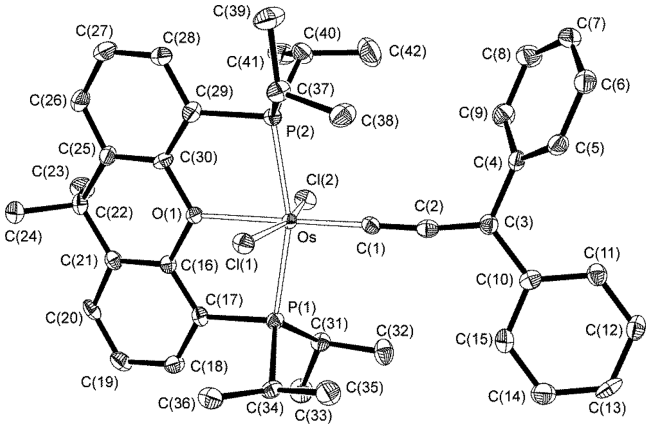


Figure 8. ORTEP diagram of complex **14** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Os−Cl(1) = 2.3842(11), Os−Cl(2) = 2.3868(12), Os−O(1) = 2.244(3), Os−P(1) = 2.3431(12), Os−P(2) = 2.3587(12), Os−C(1) = 1.851(4), C(1)−C(2) = 1.267(6), C(2)−C(3) = 1.352(6), P(1)−Os−P(2) = 162.98(4), P(1)−Os−O(1) = 81.45(8), P(2)−Os−O(1) = 81.76(8), Cl(1)−Os−Cl(2) = 165.38(4), C(1)−Os−O(1) = 179.07(16), Os−C(1)−C(2) = 179.1(4), and C(1)−C(2)−C(3) = 172.4(4).

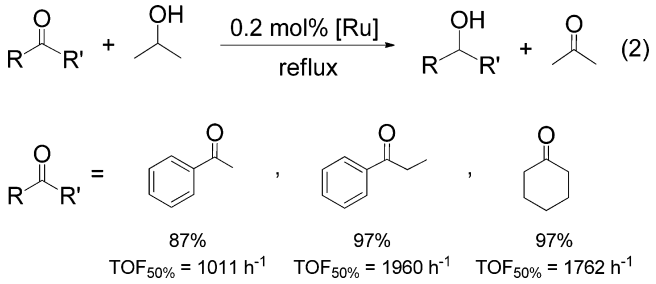
179.1(4)° and 172.4(4)°, respectively. The Os−C(1), C(1)−C(2), and C(2)−C(3) bond lengths of 1.851(4), 1.267(6), and 1.352(6) Å, respectively, compare well with those reported for the previously structurally characterized osmium-allenylidene complexes.[6b,42,46] In agreement with the presence of the allenylidene ligand, the IR spectrum contains a ν(=C=C=C) band at 1885 cm^{-1}, whereas the $^{13}C\{^1H\}$ NMR spectrum in benzene-d_6 shows triplets at 252.1, 245.5, and 156.5 ppm with C−P coupling constants of 3.5, 10.1, and 2.0 Hz, corresponding to the C_β (C(2)), C_α (C(1)), and C_γ (C(3)) atoms, respectively. A singlet at 3.0 ppm in the $^{31}P\{^1H\}$ NMR spectrum is also a characteristic feature of this compound.

Ammonia borane also reduces the C_β−C_γ double bond of the allenylidene ligand of **14** to give vinylidene compound $OsCl_2(=C=CHCHPh_2)\{xant(P^iPr_2)_2\}$ (**15**), the osmium counterpart of complex **11**. The reduction is faster than that of **10** and is completely selective. Thus, at room temperature using 1.0 equiv of ammonia borane, complex **15** was isolated as a yellow solid in 86% yield after only 4 h. The hydrogenation of the Os−C_α double bond does not take place even after 48 h in the presence of 12.0 equiv of ammonia borane (i.e., osmium favors the reduction of the C_β-C_γ double bond of the allenylidene fragment with regard to ruthenium). However, it stabilizes the M−C_α double bond, preventing the hydrogenation of the resulting vinylidene. As a consequence, it is not possible to apply a methodology similar to that described in Scheme 4 for preparing $OsH_4\{xant(P^iPr_2)_2\}$. In this context, it should be noted that osmium is not only more reducing than ruthenium but also prefers complexes with greater metal−carbon bond multiplicity.[47]

The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of **15** in benzene-d_6 are consistent with the formation of a vinylidene ligand and the structure proposed for this compound in Scheme 5. The ^1H NMR spectrum shows at 5.40 ppm a doublet (J_{H-H} = 12.0 Hz) and at 2.42 ppm a doublet of triplets (J_{H-H} = 12.0 Hz; J_{H-P} = 3.0 Hz) because of the HC(sp^3) and HC(sp^2) hydrogen atoms of the reduced cumulene. In the $^{13}C\{^1H\}$ NMR spectrum, the vinylidene C(sp^2) resonances appear at 292.8 (C_α) and 104.7 (C_β) ppm as triplets with C−P coupling constants of 9.1 and 4.2 Hz, respectively, whereas the C(sp^3) resonance is observed at 38.3 ppm also as a triplet but with a C−P coupling constant of 2.3 Hz. According to the mer coordination of the diphosphine, the $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 7.0 ppm.

Catalytic Screening for Complex 12. This hydride-tetrahydroborate complex is an efficient catalyst precursor for interesting organic reactions, including the reduction of ketones by hydrogen transfer from 2-propanol, the α-alkylation of nitriles and ketones, and the head-to-head (Z) dimerization of terminal alkynes.

The hydrogen-transfer reactions (eq 2) were performed under an argon atmosphere in 2-propanol as solvent at 80 °C using a 1:500 precursor/ketone molar ratio in the absence of any base.[48] Under these conditions, acetophenone, propiophenone, and cyclohexanone were reduced to the corresponding alcohols in high yields (87−97%) within short times, with turnover frequency values at 50% conversion ($TOF_{50\%}$) between 1011 and 1960 h^{-1}. Under the reaction conditions, complex **12** evolves into **8** (Scheme 4), which losses the coordinated hydrogen molecule under an argon atmosphere to afford the unsaturated dihydride **A**. The latter is the real catalyst of the reductions, which should take place via an innersphere mechanism[49] in four steps including (i) coordination of the ketones to **A**, (ii) formation of an alkoxy-metal intermediate by hydride migration from the metal to the carbonyl carbon atom, (iii) release of the reduced product by alkoxy exchange between the alkoxy resulting from the insertion and 2-propanol, and (iv) regeneration of **A** by a β-elimination reaction on the formed Ru−O^{i}Pr intermediate.[50]



The α-alkylation of nitriles and ketones are typical reactions within the borrowing hydrogen methodology, which provides an useful alternative to conventional alkylation reactions for the formation of C−C bonds.[22] The only waste generated through the overall process is water, which is in some cases removed from the reaction medium by using a Dean−Stark receiver. Catalysts temporally remove hydrogen from an alcohol substrate to provide an aldehyde, which undergoes a Knoevenagel condensation with the nitrile or ketone to form an alkene. The released hydrogen produces the alkene reduction, generating an overall redox-neutral process. Because the Knoevenagel condensation is base-catalyzed, the alkylation was performed in the presence of a base.[51]

Complex **12** is an efficient catalyst precursor for the alkylations of phenylacetonitrile with benzyl alcohol and 1-octanol (eq 3) and for the alkylation of acetophenone with benzyl alcohol (eq 4). The reactions were carried out in toluene as solvent with nitrile or ketone and alcohol concentrations of 0.3 M and catalyst/substrate and KOH/substrate molar ratios of 1:100 and 1:5, respectively, using a Dean−Stark receiver filled with toluene. Under these conditions, the alkylation products were obtained in 70−80% yield with $TOF_{50\%}$ values

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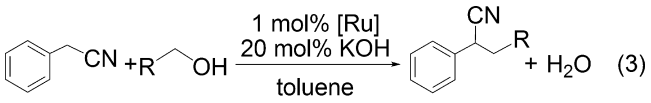
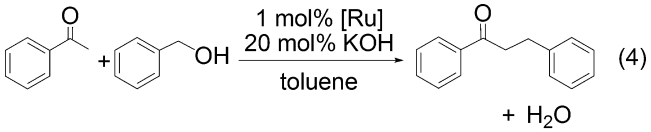
between 1.4 and 18 h^{-1}, which compare well with those obtained for the Ru,[52] Ir,[53] and Pd[54] catalysts previously described. However, they are much lower than those reported for the osmium complex [Os(η^6-*p*-cymene)(OH)(IPr)]OTf (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazolylidene and OTf = CF_3SO_3).[51]



(3)

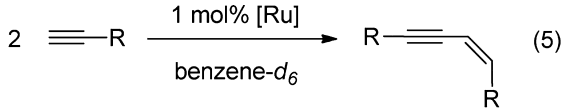
R = Ph (79%; $TOF_{50\%}$ = 18 h^{-1}), -$(CH_2)_6CH_3$ (68%; $TOF_{50\%}$ = 1.4 h^{-1})



(4)

70%; $TOF_{50\%}$ = 2.5 h^{-1}

The dimerization of terminal alkynes can give five four-carbon isomers, three enynes,[55] and two butatrienes.[56] The enynes are (E)- and (Z)-head-to-head and head-to-tail dimers. Although it is hardly achieved,[57] the regio- and stereoselective head-to-head (Z) dimerization merits particular attention because (Z)-enynes are key units found in a variety of naturally occurring anticancer drugs.[58] Like osmium-tetrahydride $OsH_4\{xant(P^iPr_2)_2\}$,[7] hydride-tetrahydroborate complex **12** is an efficient catalyst precursor for the regio- and stereoselective head-to-head (Z) dimerization of phenylacetylene and *tert*-butylacetylene in benzene-d_6 (eq 5). Although both compounds give (Z)-enynes in yields higher than 90%, complex **12** works at lower temperatures and affords higher $TOF_{50\%}$ values than the tetrahydride $OsH_4\{xant(P^iPr_2)_2\}$. Although enynes (Z)-PhC≡CCH=CHPh and (Z)-^{t}BuC≡CCH=CH^{t}Bu are formed with $TOF_{50\%}$ values of 215 and 92 h^{-1} at 80 °C in the presence of **12**, the osmium-tetrahydride needs higher temperature, 110 °C, to reach $TOF_{50\%}$ values of 100 and 30 h^{-1}, respectively. From a mechanistic point of view, no significant differences should be expected between the ruthenium and osmium precursors. Bis(alkynyl)vinylidene compounds of the type $M(C{\equiv}CR)_2(=C{=}CHR)\{xant(P^iPr_2)_2\}$, isolated in the case of osmium,[7] seem to also be the catalytic species for ruthenium. In this context, it should be mentioned that complexes $MH_2(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$ and $MH(\eta^2\text{-}H_2BH_2)(CO)(P^iPr_3)_2$ (M = Ru, Os) react with phenylacetylene in the same manner to afford the bis(alkynyl) derivatives $M(C{\equiv}CPh)_2(CO)(P^iPr_3)_2$ (M = Ru, Os).[59] The Z configuration of the dimers can be rationalized via the migratory insertion of the vinylidene into one of the M-alkynyl bonds.[7]



(5)

R = Ph (97%; $TOF_{50\%}$ = 215 h^{-1}), ^{t}Bu (92%; $TOF_{50\%}$ = 92 h^{-1})

CONCLUDING REMARKS

This work shows the entry to the chemistry of ruthenium complexes containing the POP–pincer ligand $xant(P^iPr_2)_2$, starting from the adduct *cis*-$RuCl_2\{\kappa\text{-}S\text{-}(DMSO)_4\}$, and it reveals that in contrast to $Os\{xant(P^iPr_2)_2\}$ fragment $Ru\{xant(P^iPr_2)_2\}$ avoids the oxidation state four. Although the d^4-complexes $OsH_3Cl\{xant(P^iPr_2)_2\}$ and $OsH_4\{xant(P^iPr_2)_2\}$ were obtained by reaction of $OsCl_2\{xant(P^iPr_2)_2\}(\kappa\text{-}S\text{-}DMSO)$ with molecular hydrogen in the presence of a Brønsted base, the ruthenium counterpart $RuCl_2\{xant(P^iPr_2)_2\}(\kappa\text{-}S\text{-}DMSO)$ affords the d^6-derivatives $RuHCl\{xant(P^iPr_2)_2\}(\kappa\text{-}S\text{-}DMSO)$ and $RuH_2\{xant\text{-}(P^iPr_2)_2\}(\kappa\text{-}S\text{-}DMSO)$ under the same conditions. Certainly, H_3 and H_4 species, related to $OsH_3Cl\{xant(P^iPr_2)_2\}$ and $OsH_4\{xant(P^iPr_2)_2\}$, can be prepared. However they are the dihydrogen derivatives $RuHCl(\eta^2\text{-}H_2)\{xant(P^iPr_2)_2\}$ and $RuH_2(\eta^2\text{-}H_2)\{xant(P^iPr_2)_2\}$.

The most efficient method to prepare $RuH_2(\eta^2\text{-}H_2)\text{-}\{xant(P^iPr_2)_2\}$ involves the displacement of the dimethyl sulfoxide molecule from $RuCl_2\{xant(P^iPr_2)_2\}(\kappa\text{-}S\text{-}DMSO)$ with 1,1-diphenyl-2-propyn-1-ol and the subsequent reduction of the $C_\beta{-}C_\gamma$ and $Ru{-}C_\alpha$ double bonds of the resulting ruthenium allenylidene $RuCl_2(=C{=}C{=}CPh_2)\{xant(P^iPr_2)_2\}$ with ammonia borane. The reduction leads to hydride-tetrahydroborate $RuH(\eta^2\text{-}H_2BH_2)\{xant(P^iPr_2)_2\}$, which evolves into the dihydride-dihydrogen in 2-propanol under a hydrogen atmosphere and is an efficient catalyst precursor for the hydrogen transfer from 2-propanol to ketones, the alkylations of nitriles and ketones with alcohols, and the regio- and stereoselective head-to-head (Z) dimerization of terminal alkynes.

Osmium-allenylidene complex $OsCl_2(=C{=}C{=}CPh_2)\text{-}\{xant(P^iPr_2)_2\}$ was prepared in a similar manner to its ruthenium counterpart, starting from $OsCl_2\{xant(P^iPr_2)_2\}\text{-}(\kappa\text{-}S\text{-}DMSO)$ and 1,1-diphenyl-2-propyn-1-ol. However, there are significant differences in the behavior toward ammonia borane between both compounds. Osmium favors the reduction of the $C_\beta{-}C_\gamma$ double bond of the allenylidene ligand, which is almost quantitative after 4 h with 1.0 equiv of ammonia borane, whereas 24 h and 12.0 equiv are necessary in the case of ruthenium. However, osmium stabilizes the $M{-}C_\alpha$ double bond, preventing the hydrogenation of the resulting vinylidene. As a consequence, a similar procedure to that of $RuH_2(\eta^2\text{-}H_2)\{xant(P^iPr_2)_2\}$ can not be used to prepare $OsH_4\{xant\text{-}(P^iPr_2)_2\}$.

Thus, the $Ru\{xant(P^iPr_2)_2\}$ metal fragment avoids the oxidation state four. As a result, the osmium d^4-polyhydrides are d^6-dihydrogen in the ruthenium chemistry, which require different synthetic procedures from those of osmium for their preparation.

EXPERIMENTAL SECTION

All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. 2-Propanol, acetone, and dimethyl sulfoxide (DMSO) were dried and distilled under argon. Other solvents were obtained oxygen- and water-free from an MBraun solvent-purification apparatus. NMR spectra were recorded on a Varian Gemini 2000, a Bruker ARX 300 MHz, a Bruker Avance 300 MHz, or a Bruker Avance 400 MHz instrument. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^{1}H, ^{1}H{^{31}P}, and ^{13}C{^{1}H}) or an external standard (^{31}P{^{1}H} to 85% H_3PO_4 and ^{11}B to $BF_3{\cdot}OEt_2$). Coupling constants *J* and *N* ($N = J(PH) + J(P'H)$ for ^{1}H and $N = J(PC) + J(P'C)$ for ^{13}C{^{1}H}) are given in hertz. Attenuated total reflection infrared spectra (ATR-IR) of solid samples were run on a PerkinElmer Spectrum 100 FT-IR spectrometer. C, H, N, and S analyses were carried out in a PerkinElmer 2400 CHNS/O analyzer. High-resolution electrospray mass spectra (HRMS) were acquired using a MicroTOF-Q hybrid quadrupole time-of-flight spectrometer (Bruker Daltonics). GC analysis was carried out on an Agilent 4890D series gas chromatograph with a flame ionization detector using a poly(ethylene glycol) HP Innowax column (25 m × 0.2 mm, with 0.04 μm film thickness), and GC–MS experiments were run on an Agilent 5973 mass-selective detector interfaced to an Agilent 6890

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series gas chromatograph system equipped with a 5% phenylmehylsiloxane HP-5MS column (30 m × 0.250 mm, with 0.25 μm film thickness). Acetophenone, phenylacetonitrile, benzyl alcohol, 1-octanol, phenylacetylene, *tert*-butylacetylene, and triethylamine were purchased from commercial sources and vacuum-distilled. All other reagents were purchased from commercial sources and used as received. *cis*-$RuCl_2\{\kappa\text{-}S\text{-}(DMSO)_4\}$ (**1**),[60] $RuHCl(PPh_3)_3$,[30] Ru(COD)(COT) (**9**),[61] $OsCl_2\{xant(P^iPr_2)_2\}(\kappa\text{-}S\text{-}DMSO)$ (**11**),[7] and 9,9-dimethyl-4,5-bis(diisopropylphosphino)xanthene ($xant(P^iPr_2)_2$)[1a] were prepared according to published methods.

Synthesis of $RuCl_2\{xant(P^iPr_2)_2\}(\kappa\text{-}S\text{-}DMSO)$ (2). A solution of $xant(P^iPr_2)_2$ (370 mg, 0.830 mmol) in toluene (10 mL) was added to a suspension of *cis*-$RuCl_2\{\kappa\text{-}S\text{-}(DMSO)_4\}$ (**1**) (400 mg, 0.830 mmol) in toluene (10 mL) and heated under reflux for 18 h, changing the color from pale to deep yellow. After this time, the mixture was cooled to room temperature, and the solution was concentrated to dryness. After the solvent was removed, the solid was washed with acetone (3 × 2 mL) and diethyl ether (3 × 3 mL) and was dried in vacuo. Yield: 430 mg (75%). Anal. Calcd for $C_{29}H_{46}Cl_2O_2RuSP_2$: C, 50.29; H, 6.69; S, 4.63. Found: C, 50.10; H, 6.81; S, 4.75. HRMS (electrospray, *m*/*z*): calcd for $C_{27}H_{40}ClOP_2Ru$ $[M - Cl - DMSO]^+$, 579.1285; found, 579.1378. IR (cm^{-1}): ν(O−C) 1185 (s); ν(O═S) 1090 (s). ^1H NMR (400 MHz, CD_2Cl_2, 293 K): δ 7.60 (dd, J_{H-H} = 7.6, J_{H-H} = 1.6, 2H, CH_{arom}), 7.55 (m, 2H, CH_{arom}), 7.33 (d, J_{H-H} = 7.6, 2H, CH_{arom}), 3.59 (s, 6H, $SO(CH_3)_2$), 3.12 (m, 4H, $PCH(CH_3)_2$), 1.63 (s, 6H, CH_3), 1.37 (dvt, J_{H-H} = 7.4, *N* = 15.0, 12H, $PCH(CH_3)_2$), 1.32 (dvt, J_{H-H} = 7.0, *N* = 13.2, 12H, $PCH(CH_3)_2$). $^{13}C\{^1H\}$-APT plus HSQC and HMBC NMR (100.63 MHz, CD_2Cl_2, 293 K): δ 156.2 (vt, *N* = 13.4, C_{arom}), 132.6 (vt, *N* = 5.8, C_{arom}), 132.0 (s, CH_{arom}), 128.1 (s, CH_{arom}), 124.7 (vt, *N* = 5.0, CH_{arom}), 123.3 (vt, *N* = 25.0, C_{ipso}), 51.6 (s, $SO(CH_3)_2$), 34.5 (s, $C(CH_3)_2$), 31.7 (s, $C(CH_3)_2$), 27.3 (vt, *N* = 20.8, $PCH(CH_3)_2$), 21.8 and 20.9 (both s, $PCH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (161.69 MHz, CD_2Cl_2, 293 K): δ 37.2 (s).

Synthesis of $RuHCl\{xant(P^iPr_2)_2\}(\kappa\text{-}S\text{-}DMSO)$ (3). A Fisher−Porter bottle was charged with a solution of Et_3N (127 μL, 0.909 mmol) and $RuCl_2\{xant(P^iPr_2)_2\}(\kappa\text{-}S\text{-}DMSO)$ (**2**) (300 mg, 0.433 mmol) in toluene (25 mL). The bottle was pressurized to 3 atm of H_2, and the mixture was stirred at 90 °C for 60 h, changing the color from deep to pale yellow. After the mixture was cooled to room temperature, it was filtered, and the solvent was removed in vacuo. Addition of pentane to the residue afforded a pale yellow solid, which was washed with pentane (3 × 3 mL) and dried in vacuo. Yield: 230 mg (81%). Anal. Calcd for $C_{29}H_{47}ClO_2RuP_2S$: C, 52.87; H, 7.20; S, 4.86. Found: C, 52.47; H, 7.00; S, 4.52. HRMS (electrospray, *m*/*z*): calcd for $C_{29}H_{47}O_2RuP_2S$ $[M - Cl]^+$, 623.1817; found, 623.1826. IR (cm^{-1}): ν(Ru−H) 2019 (w), ν(O−C) 1197 (s), ν(O═S) 1075 (s). ^1H NMR (400 MHz, C_6D_6, 293 K): δ 7.61 (m, 2H, CH_{arom}), 7.48 (d, J_{H-H} = 7.5, 2H, CH_{arom}), 7.26 (t, J_{H-H} = 7.5, 2H, CH_{arom}), 3.38 (s, 6H, $SO(CH_3)_2$), 2.99 (m, 2H, $PCH(CH_3)_2$), 2.71 (m, 2H, $PCH(CH_3)_2$), 1.73 (s, 3H, CH_3), 1.42 (dvt, J_{H-H} = 6.7, *N* = 12.7, 6H, $PCH(CH_3)_2$), 1.39 (dvt, J_{H-H} = 7.8, *N* = 14.3, 6H, $PCH(CH_3)_2$), 1.37 (s, 3H, CH_3), 1.36 (dvt, J_{H-H} = 7.3, *N* = 14.9, 6H, $PCH(CH_3)_2$), 1.06 (dvt, J_{H-H} = 6.8, *N* = 14.1, 6H, $PCH(CH_3)_2$), −16.53 (t, J_{H-P} = 21.7, 1H, RuH). $^{13}C\{^1H\}$-APT plus HSQC NMR (100.63 MHz, C_6D_6, 293 K): δ 157.5 (vt, *N* = 14.7, C_{arom}), 132.8 (vt, *N* = 6.0, C_{arom}), 129.8 (s, CH_{arom}), 127.0 (s, CH_{arom}), 125.0 (vt, *N* = 4.3, CH_{arom}), 124.2 (vt, *N* = 23.6, C_{ipso}), 56.4 (s, $SO(CH_3)_2$), 34.6 (s, $C(CH_3)_2$), 33.3 (s, $C(CH_3)_2$), 29.5 (vt, *N* = 14.7, $PCH(CH_3)_2$), 27.8 (vt, *N* = 28.6, $PCH(CH_3)_2$), 27.1 (s, $C(CH_3)_2$), 20.2 (s, $PCH(CH_3)_2$), 19.4 (vt, *N* = 6.0, $PCH(CH_3)_2$), 19.3 and 19.2 (both s, $PCH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (161.69 MHz, C_6D_6, 293 K): δ 54.9 (s).

Synthesis of $RuH_2\{xant(P^iPr_2)_2\}(\kappa\text{-}S\text{-}DMSO)$ (4). Method a: A Fisher−Porter bottle was charged with $RuCl_2\{xant(P^iPr_2)_2\}$-$(\kappa\text{-}S\text{-}DMSO)$ (**2**) (200 mg, 0.288 mmol), sodium hydride (69 mg, 2.880 mmol), and tetrahydrofuran (20 mL). The bottle was pressurized to 3 atm of H_2, and the mixture was stirred at 50 °C for 90 h. During this time, the color of the mixture changed from yellow to colorless. After the mixture was cooled to room temperature, it was filtered through Celite, and the resulting yellow solution was concentrated to dryness. Subsequent addition of toluene (10 mL) to the residue led to a suspension, which, after filtration through Celite, was taken to dryness. Addition of pentane to the residue afforded a pale yellow solid, which was washed with pentane and dried in vacuo. Yield: 100 mg (55%). Method b: Under a hydrogen atmosphere, a Schlenk flask equipped with a Teflon stopcock was charged with $RuH_2(\eta^2\text{-}H_2)\{xant(P^iPr_2)_2\}$ (**8**) (50 mg, 0.087 mmol), DMSO (6.2 μL, 0.087 mmol), and toluene (10 mL). The mixture was stirred at room temperature for 2 h. After the solvent was dried in vacuo, addition of pentane to the residue afforded a yellow solid that was washed with pentane and dried in vacuo. Yield: 41 mg (76%). Anal. Calcd for $C_{29}H_{48}O_2P_2RuS$: C, 55.84; H, 7.76; S, 5.14. Found: C, 55.98; H, 7.09; S, 5.41. HRMS (electrospray, *m*/*z*): calcd for $C_{29}H_{47}O_2P_2RuS$ $[M - H]^+$, 623.1817; found, 623.1802. IR (cm^{-1}): ν(Ru−H) 1928 (m), 1898 (m), ν(O−C) 1188 (s), ν(O═S) 1091 (s). ^1H NMR (400 MHz, C_6D_6, 293 K): δ 7.25 (m, 2H, CH_{arom}), 6.98 (dd, J_{H-H} = 7.4, J_{H-H} = 1.2, 2H, CH_{arom}), 6.90 (t, J_{H-H} = 7.4, 2H, CH_{arom}), 3.05 (s, 6H, $SO(CH_3)_2$), 2.57 (m, 2H, $PCH(CH_3)_2$), 2.30 (m, 2H, $PCH(CH_3)_2$), 1.45 (dvt, J_{H-H} = 7.8, *N* = 16.6, 6H, $PCH(CH_3)_2$), 1.39 (s, 3H, CH_3), 1.32 (dvt, J_{H-H} = 7.0, *N* = 14.6, 6H, $PCH(CH_3)_2$), 1.19 (dvt, J_{H-H} = 6.4, *N* = 12.4, 6H, $PCH(CH_3)_2$), 1.12 (s, 3H, CH_3), 0.97 (dvt, J_{H-H} = 7.0, *N* = 14.2, 6H, $PCH(CH_3)_2$), −10.62 (td, J_{H-P} = 30.2, J_{H-H} = 7.5, 1H, RuH), −20.70 (td, J_{H-P} = 18.6, J_{H-H} = 7.5, 1H, RuH). $^{13}C\{^1H\}$-APT NMR (100.63 MHz, C_6D_6, 293 K): δ 160.6 (vt, *N* = 14.3, C_{arom}), 135.1 (vt, *N* = 5.2, C_{arom}), 129.0 (s, CH_{arom}), 128.3 (s, CH_{arom}), 127.0 (vt, *N* = 20.7, C_{arom}), 124.3 (s, CH_{arom}), 56.9 (s, $SO(CH_3)_2$), 35.6 (s, $C(CH_3)_2$), 31.5 (s, $C(CH_3)_2$), 30.2 (vt, *N* = 12.0, $PCH(CH_3)_2$), 27.7 (vt, *N* = 32.0, $PCH(CH_3)_2$), 22.6 (s, $C(CH_3)_2$), 21.7 (vt, *N* = 12.7, $PCH(CH_3)_2$), 20.2 (s, $PCH(CH_3)_2$), 19.6 (vt, *N* = 7.6, $PCH(CH_3)_2$), 18.8 (s, $PCH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (161.69 MHz, C_6D_6, 293 K): δ 74.4 (s).

Synthesis of $RuHCl(\eta^2\text{-}H_2)\{xant(P^iPr_2)_2\}$ (5). A Fisher−Porter bottle was charged with $RuHCl\{xant(P^iPr_2)_2\}(\kappa\text{-}S\text{-}DMSO)$ (**3**) (200 mg, 0.303 mmol) and 2-propanol (20 mL). The bottle was pressurized to 3 atm of H_2, and the mixture was stirred at 110 °C for 4 weeks. During this time, the color of the mixture changed from yellow to dark brown. After cooling the mixture to room temperature, it was filtered through Celite, and the resulting yellow solution was concentrated to dryness. Addition of pentane to the residue afforded a pale beige solid, which was washed with pentane and dried in vacuo. Yield: 90 mg (51%). Anal. Calcd for $C_{27}H_{43}ClORuP_2$: C, 55.71; H, 7.45. Found: C, 55.43; H, 7.22. HRMS (electrospray, *m*/*z*): calcd for $C_{27}H_{40}ClORuP_2$ $[M - 3H]^+$, 579.1285; found, 579.1356. IR (cm^{-1}): ν(Ru−H) 2015 (w), 1930 (w), ν(O−C) 1188 (m). ^1H NMR (400 MHz, C_7D_8, 293 K): δ 7.17 (m, 2H, CH_{arom}), 7.08 (d, J_{H-H} = 7.5, CH_{arom}), 6.93 (t, J_{H-H} = 7.8, 2H, CH_{arom}), 2.68 (m, 2H, $PCH(CH_3)_2$), 2.00 (m, 2H, $PCH(CH_3)_2$), 1.63 (dvt, J_{H-H} = 7.3, *N* = 16.0, 6H, $PCH(CH_3)_2$), 1.46 (dvt, J_{H-H} = 7.0, *N* = 15.0, 6H, $PCH(CH_3)_2$), 1.34 and 1.19 (both s, 3H, CH_3), 1.08 (dvt, J_{H-H} = 7.0, *N* = 16.0, 6H, $PCH(CH_3)_2$), 0.81 (dvt, J_{H-H} = 7.4, *N* = 15.0, 6H, $PCH(CH_3)_2$), −12.28 (t, J_{H-P} = 13.2, 3H, RuH). $^{13}C\{^1H\}$-APT NMR (100.63 MHz, C_6D_6, 293 K): δ 156.3 (vt, *N* = 14.8, C_{arom}), 131.9 (vt, *N* = 5.8, C_{arom}), 130.8 and 128.3 (both s, CH_{arom}), 127.2 (vt, *N* = 21.1, C_{ipso}), 124.6 (s, CH_{arom}), 35.4 (s, $C(CH_3)_2$), 34.5 (s, $C(CH_3)_2$), 28.4 (s, $C(CH_3)_2$), 28.1 (vt, *N* = 21.8, $PCH(CH_3)_2$), 26.1 (vt, *N* = 25.8, $PCH(CH_3)_2$), 23.2 (vt, *N* = 4.7, $PCH(CH_3)_2$), 20.4 (vt, *N* = 11.5, $PCH(CH_3)_2$), 20.1 and 19.7 (both s, $PCH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (161.69 MHz, C_6D_6, 293 K): δ 72.1 (s). $t_{1(min)}$ (ms, RuH, 400 MHz, C_7D_8, 243 K): 56 ± 3 (−12.07 ppm).

Determination of the J_{H-D} Value for Complex 5. An NMR tube was charged with **5** (20 mg, 0.038 mmol), and 0.5 mL of methanol-d_4 was added. After 30 min, the ^1H NMR spectrum of this solution exhibits a multiplet with a $J_{H-D\ (average)}$ = 6.2 Hz in the hydride region.

Synthesis of $RuHCl\{xant(P^iPr_2)_2\}(PPh_3)$ (6). Method a: A solution of PPh_3 (46.5 mg, 0.100 mmol) in toluene (3 mL) was added to a suspension of $RuHCl\{xant(P^iPr_2)_2\}(\kappa\text{-}S\text{-}DMSO)$ (**3**) (50 mg, 0.080 mmol) in toluene (3 mL) and heated at 80 °C for 1 h, changing the color from pale to deep yellow. Then, the mixture was cooled to room temperature, and the solvent was removed. The pale yellow solid thus obtained was washed with acetone (2 × 1 mL) and diethyl ether (2 × 2 mL) and dried in vacuo. Yield: 40 mg (48%). Method b: A solution of $xant(P^iPr_2)_2$ (47.9 mg, 0.110 mmol)

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in toluene (5 mL) was added to a suspension of $RuHCl(PPh_3)_3$ (**7**) (100 mg, 0.100 mmol) in toluene (5 mL) and heated at 80 °C for 1 h, changing the color from dark purple to yellow. After this time, the mixture was cooled to room temperature, and the solvent was removed. The resulting pale yellow solid was washed with pentane (3 × 3 mL) and dried in vacuo. Yield: 70 mg (83%). Anal. Calcd for $C_{45}H_{56}ClOP_3Ru$: C, 64.46; H, 6.70. Found: C, 64.34; H, 6.56. HRMS (electrospray, *m*/*z*): calcd for $C_{45}H_{56}OP_3Ru$ $[M - Cl]^+$, 807.2594; found, 807.2580. IR (cm^{-1}): ν(Ru−H) 2045(w), ν(O−C) 1086 (s). ^1H NMR (300 MHz, CD_2Cl_2, 293 K): δ 8.18 (m, 6H, CH_{arom}), 7.47 (m, 2H, CH_{arom}), 7.46 (d, J_{H-H} = 7.5, 2H, CH_{arom}), 7.33 (m, 9H, CH_{arom}), 7.15 (t, J_{H-H} = 7.5, 2H, CH_{arom}), 2.30 (m, 4H, $PCH(CH_3)_2$), 1.65, 1.33 (both s, 3H, CH_3), 0.99 (dvt, J_{H-H} = 7.2, *N* = 14.6, 18H, $PCH(CH_3)_2$), 0.74 (dvt, J_{H-H} = 7.2, *N* = 15.9, 6H, $PCH(CH_3)_2$), −17.48 (dt, J_{H-P} = 27.9, J_{H-P} = 24.0, 1H, RuH). $^{13}C\{^1H\}$-APT plus HSQC and HMBC NMR (75.47 MHz, CD_2Cl_2, 293 K): δ 155.9 (vt, *N* = 14.3, C_{arom}), 140.0 (d, J_{C-P} = 42.3, C_{arom}), 135.9 (d, J_{C-P} = 10.2, CH_{arom}), 131.7 (s, C_{arom}), 130.0 and 129.2 (both s, CH_{arom}), 127.0 (d, J_{C-P} = 8.8, CH_{arom}), 126.8 (s, CH_{arom}), 126.6 (vt, *N* = 20.4, C_{ipso}), 124.3 (s, CH_{arom}), 35.1 (s, $C(CH_3)_2$), 34.4 (s, $C(CH_3)_2$), 28.9 (vt, *N* = 28.5, $PCH(CH_3)_2$), 27.6 (s, $C(CH_3)_2$), 26.6 (vt, *N* = 11.6, $PCH(CH_3)_2$), 20.9, 19.3, and 18.8 (all s, $PCH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 293 K): δ 76.4 (t, J_{P-P} = 31.2, PPh_3), 51.8 (d, J_{P-P} = 31.2, xant(P^iPr_2)$_2$).

Synthesis of $RuH_2(\eta^2\text{-}H_2)\{xant(P^iPr_2)_2\}$ (8). Method a: In a Fisher−Porter bottle, a solution of xant(P^iPr_2)$_2$ (140 mg, 0.316 mmol) in pentane (5 mL) was added to a solution of Ru(COD)(COT) (**9**) (100 mg, 0.317 mmol) in pentane (5 mL). The bottle was pressurized to 3 atm of H_2, and the mixture was stirred at room temperature for 24 h. During that time, the color of the mixture changed from bright yellow to light brown. Cooling the solution at −70 °C with a ^{i}PrOH/dry ice bath afforded the formation of a pale yellow precipitate that was washed with pentane (2 × 2 mL) and dried by passing through a stream of hydrogen gas. The complex is moderately stable under a hydrogen atmosphere. Yield: 62 mg (36%). Note that residual free xant(P^iPr_2)$_2$ was always observed. Method b: A Schlenk flask equipped with a Teflon stopcock was charged with $RuH(\eta^2\text{-}H_2BH_2)\{xant(P^iPr_2)_2\}$ (**12**) (50 mg, 0.089 mmol) and 2-propanol (3 mL). The argon atmosphere was replaced by a hydrogen atmosphere, and the mixture was stirred at 80 °C for 24 h. During that time, the color of the mixture changed from yellow to light brown. The solvent was evaporated passing a stream of hydrogen gas, and a light brown oil was thus obtained. Yield: 48 mg (94%). ^1H NMR (400 MHz, C_7D_8, 293 K): δ 7.21 (dd, J_{H-H} = 8.0, J_{H-H} = 2.0, 2H, CH_{arom}), 7.12 (m, 2H, CH_{arom}), 6.92 (t, J_{H-H} = 6.0, 2H, CH_{arom}), 2.10 (m, 4H, $PCH(CH_3)_2$), 1.33 (dvt, J_{H-H} = 6.0, *N* = 18.0, 12H, $PCH(CH_3)_2$), 1.19 (s, 6H, CH_3), 1.00 (dvt, J_{H-H} = 6.0, *N* = 14.0, 12H, $PCH(CH_3)_2$), −9.18 (t, J_{H-P} = 14.0, 4H, RuH). $^{13}C\{^1H\}$-APT NMR (75.47 MHz, C_6D_6, 293 K): δ 157.5 (vt, *N* = 15.1, C_{arom}), 132.1 (vt, *N* = 5.3, C_{arom}), 128.5 (s, CH_{arom}), 126.2 (s, CH_{arom}), 128.2 (this resonance is masked by the resonance of C_6D_6, C_{ipso}), 124.4 (vt, *N* = 3.8, CH_{arom}), 31.0 (s, $C(CH_3)_2$), 30.9 (s, $C(CH_3)_2$), 28.9 (vt, *N* = 22.6, $PCH(CH_3)_2$), 21.4 (vt, *N* = 12.8, $PCH(CH_3)_2$), 19.9 (vt, *N* = 3.8, $PCH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6, 293 K): δ 92.1 (s). $t_{1(min)}$ (ms, RuH, 400 MHz, C_7D_8, 233 K): 44 ± 3 (−8.97 ppm).

Determination of the J_{H-D} Value for Complex 8. Under a H_2 atmosphere, an NMR tube was charged with **8** (20 mg, 0.038 mmol), and 0.5 mL of benzene-d_6 was added. After 10 min, the ^1H NMR spectrum of this solution exhibits a multiplet with a $J_{H\text{-}D\ (average)}$ = 4.5 Hz in the hydride region.

Synthesis of $RuCl_2(=C=C=CPh_2)\{xant(P^iPr_2)_2\}$ (10). A solution of $RuCl_2\{xant(P^iPr_2)_2\}(\kappa\text{-}S\text{-}DMSO)$ (**2**) (400 mg, 0.577 mmol) in toluene (15 mL) was treated with 1,1-diphenyl-2-propyn-1-ol (361 mg, 1.732 mmol). The mixture was stirred under reflux overnight. During this time, the color of the mixture changed from yellow to purple. After the mixture was cooled to room temperature, the solvent was evaporated, and the addition of diethyl ether (6 mL) afforded a purple solid that was washed with diethyl ether (2 × 3 mL) and dried in vacuo. Yield: 428 mg (92%). Anal. Calcd for $C_{42}H_{50}Cl_2OP_2Ru$: C, 62.68; H, 6.26. Found: C, 62.36; H, 6.24. HRMS (electrospray, *m*/*z*): calcd for $C_{42}H_{51}Cl_2OP_2Ru$ $[M + H]^+$, 805.1836; found, 805.1870. IR (cm^{-1}): ν(C=C=C) 1889 (s), ν(O−C) 1187 (s). ^1H NMR (300 MHz, C_6D_6, 293 K): δ 8.25−7.01 (m, 16H, CH_{arom}), 3.12 (m, 4H, $PCH(CH_3)_2$), 1.58 (dvt, J_{H-H} = 6.0, *N* = 15.0, 12H, $PCH(CH_3)_2$), 1.47 (dvt, J_{H-H} = 9.0, *N* = 15.0, 12H, $PCH(CH_3)_2$), 1.40 (s, 6H, CH_3). $^{13}C\{^1H\}$-APT plus HSQC and HMBC NMR (75.47 MHz, C_6D_6, 293 K): δ 308.8 (t, J_{C-P} = 12.8, Ru=C), 253.5 (s, =C=), 154.8 (vt, *N* = 14.3, C_{arom}-xant(P^iPr_2)$_2$), 147.3 (s, =CPh_2), 145.8 (s, C_{ipso}), 133.9 (s, CH_{arom}-xant(P^iPr_2)$_2$), 132.1 (vt, *N* = 5.3, C_{arom}-xant(P^iPr_2)$_2$), 129.7 and 129.1 (both s, CH_{arom}), 129.0 (s, CH_{arom}-xant(P^iPr_2)$_2$), 126.6 (s, CH_{arom}), 124.5 (vt, *N* = 24.9, C_{ipso}-xant(P^iPr_2)$_2$), 124.0 (vt, *N* = 4.5, CH_{arom}-xant(P^iPr_2)$_2$), 34.4 (s, $C(CH_3)_2$), 33.5 (s, $C(CH_3)_2$), 25.0 (vt, *N* = 22.6, $PCH(CH_3)_2$), 22.1, 19.6 (both s, $PCH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6, 293 K): δ 46.9 (s).

Spectroscopic Detection of $RuCl_2(=C=CH-CHPh_2)\{xant(P^iPr_2)_2$ (11). A solution of $RuCl_2(=C=C=CPh_2)\{xant(P^iPr_2)_2\}$ (**10**) (100 mg, 0.124 mmol) in toluene (10 mL) was treated with ammonia borane (11.5 mg, 0.373 mmol). After stirring the mixture at room temperature for 24 h, it was dried in vacuo and dissolved in benzene-d_6. ^1H and $^{31}P\{^1H\}$ NMR spectroscopies show a 1:3 mixture of complexes **10** and **11**. Spectroscopic data for **11**: ^1H NMR (300 MHz, C_6D_6, 293 K): δ 8.14−6.84 (16H, CH_{arom}), 5.60 (d, J_{H-H} = 10.5, 1H, −$CHPh_2$), 4.68 (dt, J_{H-H} = 10.5, J_{H-P} = 3.0, 1H, =CH−), 3.02 (m, 4H, $PCH(CH_3)_2$), 1.49 (dvt, J_{H-H} = 7.5, *N* = 16.5, 12H, $PCH(CH_3)_2$), 1.39 (dvt, J_{H-H} = 6.0, *N* = 15.0, 12H, $PCH(CH_3)_2$), 1.20 (s, 6H, CH_3). $^{13}C\{^1H\}$-APT NMR plus HSQC and HMBC (75.47 MHz, C_6D_6, 293 K): δ 346.4 (t, J_{C-P} = 12.8, Ru=C), 153.9 (vt, *N* = 12.8, C_{arom}-xant(P^iPr_2)$_2$), 146.6 (s, C_{ipso}), 133.7 (s, CH_{arom}-xant(P^iPr_2)$_2$), 131.6 (vt, *N* = 5.3, C_{arom}-xant(P^iPr_2)$_2$), 129.4 (s, CH_{arom}-xant(P^iPr_2)$_2$), 128.4 and 128.2 (both s, CH_{arom}), 124.3 (vt, N = 24.2, C_{ipso}-xant(P^iPr_2)$_2$), 125.9 (s, CH_{arom}), 123.7 (vt, *N* = 5.3, CH_{arom}-xant(P^iPr_2)$_2$), 106.9 (t, J_{C-P} = 3.0, =CH−), 41.7 (s, −$CHPh_2$), 34.0 (s, $C(CH_3)_2$), 32.9 (s, $C(CH_3)_2$), 25.7 (vt, *N* = 21.9, $PCH(CH_3)_2$), 22.2 and 19.7 (both s, $PCH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6, 293 K): δ 37.3 (s).

Synthesis of $RuH(\eta^2\text{-}H_2BH_2)\{xant(P^iPr_2)_2\}$ (12). A solution of $RuCl_2(=C=C=CPh_2)\{xant(P^iPr_2)_2\}$ (**10**) (100 mg, 0.124 mmol) in toluene (12 mL) was treated with ammonia borane (46 mg, 1.491 mmol). The mixture was stirred at room temperature for 48 h, and the color of the mixture changed from purple to yellow. After this time, it was filtered through Celite, and the yellow solution obtained was dried in vacuo. Pentane (10 mL) was added to afford a yellow solid that was washed with pentane and dried in vacuo. Yield: 52 mg (75%). Anal. Calcd for $C_{27}H_{45}BOP_2Ru$: C, 57.96; H, 8.11. Found: C, 58.16; H, 8.17. HRMS (electrospray, *m*/*z*): calcd for $C_{27}H_{40}OP_2Ru$ $[M - H_2BH_2 - H]^+$, 543.1522; found, 543.1512. IR (cm^{-1}): ν(B−H) 2389, 2321, ν(Ru−H) 1945 (m), ν(O−C) 1180 (s). ^1H NMR (400 MHz, C_7D_8, 293 K): δ 7.26−6.82 (m, 6H, CH_{arom}), 2.80 (m, 2H, $PCH(CH_3)_2$), 2.45 (m, 2H, $PCH(CH_3)_2$), 1.36 (dvt, J_{H-H} = 8.0, *N* = 16.0, 6H, $PCH(CH_3)_2$), 1.32 (s, 3H, CH_3), 1.28 (dvt, J_{H-H} = 6.0, *N* = 14.0, 6H, $PCH(CH_3)_2$), 1.20 (dvt, J_{H-H} = 8.0, *N* = 12.0, 6H, $PCH(CH_3)_2$), 1.15 (dvt, J_{H-H} = 6.0, *N* = 14.0, 6H, $PCH(CH_3)_2$), 0.94 (s, 3H, CH_3), −4.86 (br, 1H, Ru−H_a-B), −15.41 (td, J_{H-P} = 20.0, J_{H-H} = 8.0, 1H, RuH), −24.08 (br, 1H, Ru−H_b-B). ^1H NMR (400 MHz, C_7D_8, 243 K): δ 7.15−6.85 (6H, CH_{arom}), 6.08 (br, 2H, H_2-B-H_2), 2.82 (m, 2H, $PCH(CH_3)_2$), 2.41 (m, 2H, $PCH(CH_3)_2$), 1.36 (dvt, J_{H-H} = 10.0, *N* = 16.0, 6H, $PCH(CH_3)_2$), 1.27 (dvt, J_{H-H} = 8.0, *N* = 16.0, 6H, $PCH(CH_3)_2$), 1.21 (s, 3H, CH_3), 1.17 and 1.14 (both dvt, overlapped, 12H, $PCH(CH_3)_2$), 0.88 (s, 3H, CH_3), −4.77 (br, 1H, Ru−H_a−B), −15.35 (td, J_{H-P} = 20.0, J_{H-H} = 8.0, 1H, RuH), −23.92 (br, 1H, Ru−H_b−B). $^1H\{^{31}P\}$ NMR (400 MHz, C_7D_8, 293 K, high-field region): δ −4.85 (br, 1H, Ru−H_a−B), −15.41 (d, J_{H-H} = 8.0, 1H, RuH), −24.07 (br, 1H, Ru−H_b−B). $^{13}C\{^1H\}$-APT NMR (75.47 MHz, C_6D_6, 293 K): δ 158.5 (vt, *N* = 13.6, C_{arom}), 132.7 (vt, *N* = 6.0, C_{arom}), 129.7 (s, CH_{arom}), 128.1 (this resonance is masked by the resonance of C_6D_6, C_{ipso}), 125.5 (s, CH_{arom}), 124.8 (vt, *N* = 3.8, CH_{arom}), 34.9 (s, $C(CH_3)_2$), 34.5 (s, $C(CH_3)_2$), 26.1 (vt, *N* = 16.6, $PCH(CH_3)_2$), 24.0 (s, $C(CH_3)_2$), 23.9 (vt, *N* = 25.7, $PCH(CH_3)_2$), 20.1 (vt, *N* = 3.8, $PCH(CH_3)_2$), 19.6 and 19.5 (both vt, overlapped, $PCH(CH_3)_2$),

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17.5 (s, PCH(CH_3)$_2$). ^{31}P{^{1}H} NMR (121.5 MHz, C_7D_8, 293 K): δ 69.5 (s). ^{11}B{^{1}H} NMR (128.38 MHz, C_7D_8, 293 K): δ 31.7 (br, H_2BH_2).

Synthesis of OsCl$_2$(=C=C=CPh$_2$){xant(P^{i}Pr$_2$)$_2$} (14). A solution of OsCl$_2$(xant(P^{i}Pr$_2$)$_2$)(κ-*S*-DMSO) (**13**) (400 mg, 0.512 mmol) in toluene (15 mL) was treated with 1,1-diphenyl-2-propyn-1-ol (320 mg, 1.535 mmol). The mixture was stirred under reflux overnight. During this time, the color of the mixture changed from orange to bright yellow. After the mixture was cooled to room temperature, the solvent was evaporated and the addition of diethyl ether (6 mL) afforded a yellow solid which was washed with diethyl ether (2 × 3 mL) and dried in vacuo. Yield: 375 mg (82%). Anal. Calcd for $C_{42}H_{50}Cl_2OOsP_2$: C, 56.43; H, 5.64. Found: C, 56.25; H, 5.52. HRMS (electrospray, *m*/*z*): calcd for $C_{42}H_{51}Cl_2OOsP_2$ [M + H]$^+$, 895.2384; found, 895.2401. IR (cm^{-1}): ν(C=C=C) 1885 (s); ν(O−C) 1184 (s). ^{1}H NMR (400 MHz, C_6D_6, 293 K): δ 7.96−6.82 (m, 16H, CH_{arom}), 3.19 (m, 4H, PC*H*(CH$_3$)$_2$), 1.57 (dvt, J_{H-H} = 8.0, *N* = 16.0, 12H, PCH(C*H*$_3$)$_2$), 1.40 (dvt, J_{H-H} = 8.0, *N* = 16.0, 12H, PCH(C*H*$_3$)$_2$), 1.21 (s, 6H, C*H*$_3$). ^{13}C{^{1}H}-APT plus HSQC and HMBC NMR (100.63 MHz, C_6D_6, 293 K): δ 252.1 (t, J_{C-P} = 3.5, =C=), 245.5 (t, J_{C-P} = 10.1, Os=C), 156.5 (t, J_{C-P} = 2.0, =CPh$_2$), 156.3 (vt, *N* = 12.1, C_{arom}-xant(P^{i}Pr$_2$)$_2$), 134.8 (s, CH_{arom}-xant(P^{i}Pr$_2$)$_2$), 132.3 (vt, *N* = 6.0, C_{arom}-xant(P^{i}Pr$_2$)$_2$), 130.2 (s, CH_{arom}-xant(P^{i}Pr$_2$)$_2$), 129.6 (s, CH_{arom}), 128.3 (this resonance is masked by the resonance of C_6D_6, C_{ipso}-xant(P^{i}Pr$_2$)$_2$), 127.4 and 127.3 (both s, CH_{arom}), 125.5 (s, C_{ipso}), 124.9 (vt, *N* = 5.0, CH_{arom}-xant(P^{i}Pr$_2$)$_2$), 34.6 (s, *C*(CH$_3$)$_2$), 34.0 (s, C(*C*H$_3$)$_2$), 25.5 (vt, *N* = 25.2, PCH(CH$_3$)$_2$), 22.7 (s, PCH(*C*H$_3$)$_2$), 19.8 (s, PCH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6, 293 K): δ 3.0 (s).

Synthesis of OsCl$_2$(=C=CH−CHPh$_2$){xant(P^{i}Pr$_2$)$_2$ (15). A solution of OsCl$_2$(=C=C=CPh$_2$){xant(P^{i}Pr$_2$)$_2$} (**14**) (150 mg, 0.168 mmol) in toluene (8 mL) was treated with ammonia borane (5.2 mg, 0.168 mmol). The mixture was stirred at room temperature for 4 h. During this time, the color of the mixture changed from bright yellow to yellow. After the solvent was evaporated, the addition of diethyl ether (6 mL) afforded a yellow solid that was washed with diethyl ether (2 × 3 mL) and dried in vacuo. Yield: 130 mg (86%). Anal. Calcd for $C_{42}H_{52}Cl_2OOsP_2$: C, 56.30; H, 5.85. Found: C, 56.03; H, 5.82. HRMS (electrospray, *m*/*z*): calcd for $C_{42}H_{51}Cl_2OOsP_2$ [M − H]$^+$, 895.2384; found, 895.2413. IR (cm^{-1}): ν(Os=C=C) 1676 (s), ν(O−C) 1178 (s). ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 7.98−6.81 (m, 16H, CH_{arom}), 5.40 (d, J_{H-H} = 12.0, 1H, −C*H*Ph$_2$), 3.23 (m, 4H, PC*H*(CH$_3$)$_2$), 2.42 (dt, J_{H-H} = 12.0, J_{H-P} = 3.0, 1H, =CH−), 1.58 (dvt, J_{H-H} = 9.0, *N* = 15.0, 12H, PCH(C*H*$_3$)$_2$), 1.40 (dvt, J_{H-H} = 9.0, *N* = 15.0, 12H, PCH(C*H*$_3$)$_2$), 1.17 (s, 6H, CH$_3$). ^{13}C{^{1}H}-APT plus HSQC and HMBC NMR (75.47 MHz, C_6D_6, 293 K): δ 292.8 (t, J_{C-P} = 9.1, Os=C), 155.5 (vt, *N* = 12.1, C_{arom}-xant(P^{i}Pr$_2$)$_2$), 148.9 (t, J_{C-P} = 1.5, C_{ipso}), 134.6 (s, CH_{arom}-xant(P^{i}Pr$_2$)$_2$), 131.9 (vt, *N* = 6.0, C_{arom}-xant(P^{i}Pr$_2$)$_2$), 129.7 (s, CH_{arom}-xant(P^{i}Pr$_2$)$_2$), 128.5 (s, CH_{arom}), 127.1 (s, CH_{arom}), 126.9 (vt, *N* = 29.4, C_{ipso}-xant(P^{i}Pr$_2$)$_2$), 125.9 (s, CH_{arom}), 124.4 (vt, *N* = 6.0, CH_{arom}-xant(P^{i}Pr$_2$)$_2$), 104.7 (t, J_{C-P} = 4.2, =CH−), 38.3 (t, J_{C-P} = 2.3, −CHPh$_2$), 34.2 (s, *C*(CH$_3$)$_2$), 33.5 (s, C(CH$_3$)$_2$), 25.5 (vt, *N* = 25.7, PCH(CH$_3$)$_2$), 22.5 (s, PCH(CH$_3$)$_2$), 19.8 (vt, *N* = 2.3, PCH(CH$_3$)$_2$). ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6, 293 K): δ 7.0 (s).

Hydrogen Transfer from 2-Propanol to Ketones Catalyzed by RuH(η^2-H$_2$BH$_2$){xant(P^{i}Pr$_2$)$_2$} (12). Under an argon atmosphere, ruthenium complex **12** (5.4 mg, 0.010 mmol) and the corresponding ketone (5 mmol) were dissolved in 8 mL of 2-propanol in a two-necked flask fitted with a condenser. The second neck was capped with a Suba seal to allow samples to be taken by syringe without opening the system. The reaction mixture was stirred at 80 °C for the indicated time. The course of the reaction was monitored by GC analysis.

α-Alkylation of Nitriles and Ketones with Alcohols by RuH(η^2-H$_2$BH$_2$){xant(P^{i}Pr$_2$)$_2$} (12). Under an argon atmosphere, complex **12** (8.4 mg, 0.015 mmol), KOH (19.8 mg, 0.300 mmol), the corresponding nitrile or ketone (1.50 mmol), the corresponding alcohol (1.50 mmol), pentadecane (69 μL, 0.25 mmol) as internal standard (in the case of *n*-octanol, this reagent was used as internal standard too, using the signal corresponding to the terminal methyl group as reference), and 10 mL of toluene were introduced in a two-necked flask fitted with a Dean−Stark receiver filled with toluene and fitted with a condenser. The second neck was capped with a Suba seal to allow samples to be taken by syringe without opening the system. The flask was placed under a thermostatic bath at 110 °C and kept stirring for the determined time. The course of the reaction was monitored by ^{1}H NMR, taking samples of 0.5 mL of the reaction mixture and quantifying the appearance of the corresponding coupling compound. ^{1}H NMR spectra of the coupling products agree with those previously reported for 2,3-diphenylpropanenitrile, 2-phenyldecanenitrile, and 1,3-diphenylpropan-1-one.[51]

Dimerization of Terminal Alkynes Catalyzed by RuH(η^2-H$_2$BH$_2$){xant(P^{i}Pr$_2$)$_2$} (12). A screw-top NMR tube charged with a solution of terminal alkyne (HC≡CR, R = Ph or ^{t}Bu; 1 mmol) and compound **12** (5.4 mg, 0.010 mmol) in benzene-d_6 was placed into a thermostatic bath at 80 °C, and the reaction was monitored by ^{1}H NMR spectroscopy using dioxane as internal standard. TOF was determined at 50% conversion. After the completion of the reaction, the solvent was removed, and pentane was added to the crude product. The solution was filtered through silica gel and analyzed by ^{1}H NMR spectroscopy. ^{1}H NMR spectra of the isolated products agree with those previously reported for (*Z*)-PhCH=CHC≡CPh and (*Z*)-^{t}BuCH=CHC≡C^{t}Bu.[7]

Structural Analysis of Complexes 2−4, 10, and 14. Crystals of all complexes were obtained by slow diffusion of pentane to saturated solutions in THF. X-ray data were collected for the complexes on a Bruker Smart APEX diffractometer equipped with a normal focus and 2.4 kW sealed-tube source (Mo radiation, λ = 0.71073 Å) operating at 50 kV and 40 mA (**3**, **4**, **10**, and **14**) or 30 mA (**2**). Data were collected over the complete sphere. Each frame exposure time was 10 s (**14**), 20 s (**2**−**4**), or 30 s (**10**), covering 0.3° in ω. Data were corrected for absorption by using a multiscan method applied with the SADABS program.[62] The structures were solved by Patterson or direct methods and refined by full-matrix least-squares on F^2 with SHELXL97,[63] including isotropic and subsequently anisotropic displacement parameters. The hydrogen atoms (except hydrides) were observed in the least Fourier maps or calculated and were refined freely or using a restricted riding model. Hydrides were observed in the last cycles of refinement and refined freely for **4**, but for **2** and **3**, they refined too close to metals, so a restricted refinement model was used.

Crystal data for **2**: $C_{29}H_{46}Cl_2O_2P_2RuS$, M_w 692.63, orange, irregular block (0.24 × 0.08 × 0.08), monoclinic, space group $P2_1/c$, *a*: 12.2001(7) Å, *b*: 13.8477(8) Å, *c*: 18.6741(11) Å, β: 101.9140(10)°, *V* = 3086.9(3) Å^3, *Z* = 4, *Z*′ = 1, D_{calc}: 1.490 g cm^{-3}, F(000): 1440, *T* = 100(2) K, μ 0.878 mm^{-1}. 36 652 measured reflections (2θ: 3−58°, ω scans 0.3°), 7379 unique (R_{int} = 0.0500), min/max transm. factors 0.725/0.842. Final agreement factors were R^1 = 0.0341 (5683 observed reflections, $I > 2\sigma(I)$) and wR^2 = 0.0847; data/restraints/parameters 7379/10/345; GoF = 1.006. Largest peak and hole 0.875 and −0.492 e/ Å^3.

Crystal data for **3**: $C_{29}H_{47}ClO_2P_2RuS$, M_w 658.19, yellow, irregular block (0.14 × 0.12 × 0.10), orthorhombic, space group $P2_12_12_1$, *a*: 10.652(3) Å, *b*: 12.276(4) Å, *c*: 23.675(7) Å, *V* = 3095.8(16) Å^3, *Z* = 4, *Z*′ = 1, D_{calc}: 1.412 g cm^{-3}, F(000): 1376, *T* = 100(2) K, μ 0.788 mm^{-1}). 38 404 measured reflections (2θ: 3−58°, ω scans 0.3°), 7623 unique (R_{int} = 0.0876); min/max transm. factors 0.738/0.931. Final agreement factors were R^1 = 0.0447 (6234 observed reflections, $I > 2\sigma(I)$) and wR^2 = 0.0857; Flack parameter 0.02(3); data/restraints/parameters 7623/1/342; GoF = 0.988. Largest peak and hole 1.092 and −0.441 e/ Å^3.

Crystal data for **4**: $C_{29}H_{48}O_2P_2RuS$, M_w 623.74, yellow, prism (0.18 × 0.10 × 0.06), orthorhombic, space group $P2_12_12_1$, *a*: 11.3942(8) Å, *b*: 12.0436(9) Å, *c*: 22.0937(16) Å, *V* = 3031.9(4) Å^3, *Z* = 4, *Z*′ = 1, D_{calc}: 1.366 g cm^{-3}, F(000): 1312, *T* = 100(2) K, μ 0.715 mm^{-1}. 36 800 measured reflections (2θ: 3−58°, ω scans 0.3°), 7328 unique (R_{int} = 0.0554); min/max transm. factors 0.789/0.862. Final agreement factors were R^1 = 0.0371 (6544 observed reflections, $I > 2\sigma(I)$) and wR^2 = 0.0847; Flack parameter 0.49(3); data/restraints/parameters 7328/0/337; GoF = 1.074. Largest peak and hole 1.689 and −0.610 e/ Å^3.

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Crystal data for **10**: $C_{42}H_{50}Cl_2OP_2Ru$, M_w 804.73, red, plate (0.18 × 0.15 × 0.03), monoclinic, space group $P2_1/c$, a: 13.3598(17) Å, b: 14.0823(18) Å, c: 39.586(5) Å, β: 92.453(2)°, V = 7440.7(16) Å^3, Z = 8, Z' = 2, D_{calc}: 1.437 g cm^{-3}, F(000): 3344, T = 100(2) K, μ 0.684 mm^{-1}. 54 957 measured reflections (2θ: 3−58°, ω scans 0.3°), 13 842 unique (R_{int} = 0.1031); min/max transm. factors 0.739/0.862. Final agreement factors were R^1 = 0.0751 (9543 observed reflections, $I > 2\sigma(I)$) and wR^2 = 0.1581; data/restraints/parameters 13842/0/885; GoF = 1.074. Largest peak and hole 0.850 and −1.160 e/ Å^3.

Crystal data for **14**: $C_{42}H_{50}Cl_2OOsP_2$, M_w 893.86, red, irregular block (0.37 × 0.16 × 0.05), orthorhombic, space group $Pca2_1$, a: 22.2729(12) Å, b: 14.7254(8) Å, c: 11.6178(6) Å, V = 3810.4(4) Å^3, Z = 4, Z' = 1, D_{calc}: 1.558 g cm^{-3}, F(000): 1800, T = 100(2) K, μ 3.603 mm^{-1}. 44 778 measured reflections (2θ: 3−58°, ω scans 0.3°), 9049 unique (R_{int} = 0.0413); min/max transm. factors 0.725/0.862. Final agreement factors were R^1 = 0.0279 (7640 observed reflections, $I > 2\sigma(I)$) and wR^2 = 0.0660; Flack parameter 0.001(7); data/restraints/parameters 9049/1/443; GoF = 1.008. Largest peak and hole 1.403 and −0.917e/ Å^3.

Computational Details. The theoretical calculations were carried out by optimizing the structures at the m06-DFT[64] levels with the Gaussian 09 program.[65] The basis sets used were LANL2DZ basis and pseudopotentials for Ru and 6-31G** for the rest of the atoms. We fully optimized these structures and calculated Gibbs free energies. All stationary points were confirmed by having only positive vibrational frequencies.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

High-field region of the $^1H\{^{31}P\}$ NMR spectra of partially deuterated complexes **5** and **8**; ^1H NMR spectra of complexes **4** and **12**; ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$-APT NMR spectra of complex **11**; full ref 65; computational details; optimized coordinates and energies of all optimized structures; and CIF crystallographic data for compounds **2**−**4**, **10**, and **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: maester@unizar.es.

Notes

The authors declare no competing financial interest.

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