Osmium-Catalyzed Allylic Alkylation

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Received May 21, 2008

Complex $[OsCl_2(\eta^6\text{-}p\text{-cymene})]_2$ (**1**) reacts with (5,7-dioxa-6-phosphadibenzo[*a*,*c*]cyclohepten-6-yl)-dimethylamine (L^1) and (−)-(*R*)-(3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]dinaphthalen-4-yl)dimethylamine (L^2) to give $OsCl_2(\eta^6\text{-}p\text{-cymene})L$ ($L = L^1$ (**2**), L^2 (**3**)). Complexes **1**−**3** and $OsCl_2(\eta^6\text{-}p\text{-cymene})\{P(OPh)_3\}$ (**4**) are efficient catalyst precursors for the alkylation of 1-phenylallyl methylcarbonate (**5a**), 1-phenylallyl acetate (**5b**), cinnamyl methylcarbonate (**6a**), and cinnamyl acetate (**6b**) with sodium dimethylmalonate to afford 1-phenylallyl dimethylmalonate (**7**) and cinnamyl dimethylmalonate (**8**) with branched:linear molar ratios between 97:3 and 67:33. In the absence of sodium dimethylmalonate, the reaction of **1** with **5a** leads initially to $\{OsCl(\eta^6\text{-}p\text{-cymene})\}_2(\mu\text{-OMe})_2$ (**9**) and subsequently to $[\{Os(\eta^6\text{-}p\text{-cymene})\}_2(\mu\text{-OMe})_3][O_2COMe]$ (**10**). In the absence of **5a**, the reaction of **1** with sodium dimethylmalonate gives $Os\{\kappa^1\text{-}C^3\text{-}[CH(CO_2Me)_2]\}\{\kappa^2\text{-}O,O\text{-}[CH(CO_2Me)_2]\}(\eta^6\text{-}p\text{-cymene})$ (**11**). Complexes **9**−**11** are also efficient catalyst precursors for the alkylation of **5a** with sodium dimethylmalonate. The activity of **9** and **10** is the same as that of **1**. However, complex **11** is significantly less efficient than **1**. In contrast to the latter, complexes **2** and **3** do not react with **5a** in the absence of sodium dimethylmalonate. In the absence of the substrate, the reactions of **2** and **3** with sodium dimethylmalonate lead to $Os\{\kappa^1\text{-}C^3\text{-}[CH(CO_2Me)_2]\}Cl(\eta^6\text{-}p\text{-cymene})L$ ($L = L^1$ (**12**), L^2 (**13**)), which further react with excess sodium dimethylmalonate to give **11**. The catalytic behavior of **12** and **13** has been also studied. Their activities are the same as those of **2** and **3** and intermediate between those of **10** and **11**. Complexes **3**, **9**, **11**, and **12** have been characterized by X-ray diffraction analysis.

Introduction

Osmium is more reducing than ruthenium and prefers coordination saturation and redox isomers with more metal−carbon bonds.[1] This is the reason for a more versatile stoichiometric osmium chemistry.[2] However it appears to be a handicap from a catalytic point of view. Thus, the catalytic osmium chemistry is poor.[3] In addition to the Sharpless' osmium-catalyzed asymmetric olefin dihydroxylation,[4] a few homogeneous catalytic processes promoted by osmium complexes have been reported. They include reduction of organic substrates,[5] addition of silanes to alkynes,[6] dehalogenation of polychloroarenes,[7] dimerization of terminal alkynes to butatrienes,[8] polymerization of alkynes,[9] ring-opening metathesis polymerization of norbornene, 2,5-norbornadiene, and cyclooctadiene,[10] ring-closing and cross metathesis,[11] cyclopropanation of olefins,[12] Diels−Alder reactions,[13] Tishchenko dimerization and trimerization of aldehydes,[14] etherification of ketones, aldehydes, and alcohols,[15] and oxidation of alcohols.[16]

Allylic alkylation is among the most successful catalytic C−C bond formation in organic chemistry.[17] From a mechanistic point of view, these reactions occur via electrophilic π-allyl intermediates so that both branched and linear substrates can yield branched and linear products (Scheme 1). The regioselectivity of the processes is a difficult problem and a challenge in the field. A variety of transition metal complexes have been used

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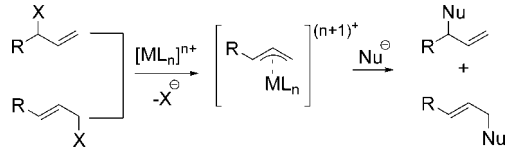
10.1021/om800460h CCC: $40.75
Publication on Web 09/09/2008

Scheme 1



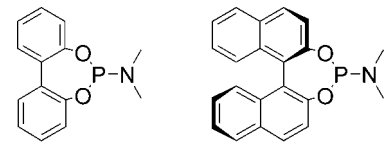
as catalysts, and the metal center appears to determine the regioselectivity of the addition. Thus, palladium-catalyzed reactions tend to cause nucleophilic addition at the less sterically hindered allylic terminus, giving rise to linear-type products,[18] although ligands can affect the selectivity.[19] In contrast to palladium, complexes of other metals such as tungsten,[20] molybdenum,[21] iron,[22] ruthenium,[23] rhodium,[24] iridium,[25] nickel,[26] platinum,[27] and copper[28] preferentially yield branched-type products, by attack at the more hindered allylic terminus.

Osmium catalysts for the allylic substitution are unknown. As a part of our work on the osmium organometallic chemistry field, in this paper, we report the preparation and characterization of the first osmium organometallic catalytic precursors for allylic alkylation reactions.

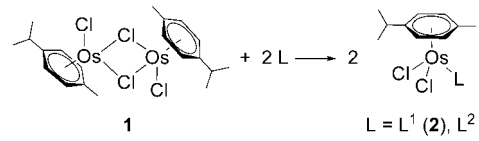
Results and Discussion

1. Preparation of $OsCl_2(\eta^6$-*p*-cymene)(phosphoramidite) Complexes. Among the monodentate phosphorus donor ligands used in allylic substitution reactions, phosphoramidites occupy a prominent place[29] due to their π-acceptor capacity, which enhances the electrophilicity of the allyl intermediates. Thus, in order to initiate an exploration on osmium systems with this type of ancillary, we have selected (5,7-dioxa-6-phosphadibenzo[*a*,*c*]cycloheptен-6-yl)dimethylamine[30] (L^1) and (−)-(*R*)-(3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*]dinaphthalen-4-yl)dimethylamine (L^2)[31] by their easy preparations, as examples of achiral and chiral ligands, respectively (Chart 1).

Chart 1



Treatment at room temperature of toluene suspensions of the dimer $[OsCl_2(\eta^6$-*p*-cymene)$]_2$ (**1**) with 2.0 equiv of the phosphoramidites L^1 and L^2 leads after 18 h to the mononuclear derivatives $OsCl_2(\eta^6$-*p*-cymene)L^1 (**2**) and $OsCl_2(\eta^6$-*p*-cymene)L^2 (**3**). These compounds, which are the first osmium complexes containing a phosphoramidite ligand, are isolated as orange solids in 77% and 52% yield, respectively, according to eq 1.



(1)

Complex **3** has been characterized by an X-ray crystallographic study. The structure has two chemically equivalent but crystallographically independent molecules in the asymmetric unit. A drawing of one of them is shown in Figure 1. The geometry around the osmium atom is close to octahedral with the arene occupying three sites of a face. The angles Cl(1)−Os(1)−Cl(2), Cl(1)−Os(1)−P(1), and Cl(2)−Os(1)−P(1) are 84.31(7)° and 83.90(7)°, 90.72(7)° and 90.98(7)°, and 89.41(7)° and 89.69(7)°, respectively.

In agreement with the presence of the phosphoramidite ligand in these complexes, their $^{31}P\{^1H\}$ NMR spectra in dichloromethane-d_2 at room temperature show singlets at 121.5 (**2**) and 108.3 (**3**) ppm.

2. Allylic Alkylation. The dimer **1**, the mononuclear phosphoramidite derivatives **2** and **3**, and the previously reported triphenylphosphite complex $OsCl_2(\eta^6$-*p*-cymene)$\{P(OPh)_3\}$[32] (**4**)

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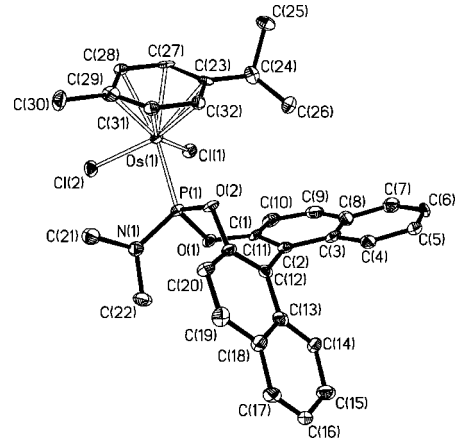
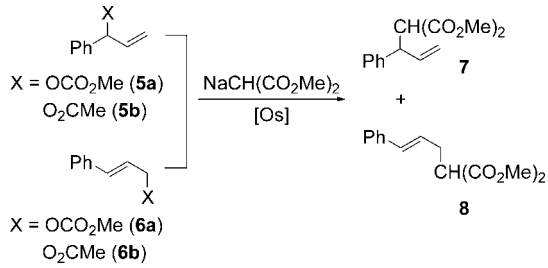
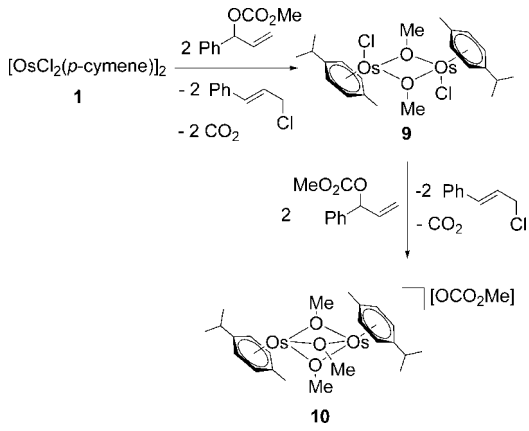


Figure 1. Molecular diagram of complex **3**. Selected bond lengths (Å) and angles (deg): Os(1)−Cl(1) 2.4000(19) and 2.4056(19), Os(1)−Cl(2) 2.407(2) and 2.410(2), Os(1)−P(1) 2.284(2) and 2.287(2); Cl(1)−Os(1)−Cl(2) 84.31(7) and 83.90(7), Cl(1)−Os(1)−P(1) 90.72(7) and 90.98(7), Cl(2)−Os(1)−P(1) 89.41(7) and 89.69(7).

Scheme 2



Scheme 3



are efficient catalyst precursors for the alkylation of the racemic branched substrates 1-phenylallyl methylcarbonate (**5a**) and 1-phenylallyl acetate (**5b**) and the linear derivates cinnamyl methylcarbonate (**6a**) and cinnamyl acetate (**6b**), with sodium dimethylmalonate, to afford both 1-phenylallyl dimethylmalonate (**7**) and cinnamyl dimethylmalonate (**8**), according to Scheme 2. The reactions were carried out in tetrahydrofuran at 60 °C, using a 1:2 substrate:nucleophile molar ratio and 4 mol % of osmium. Yields and branched:linear molar ratios of products are given in Table 1.

Complex **1** is a more efficient catalyst precursor than the phosphorus derivatives **2**−**4**. This suggests that the phosphorus donor ligands block coordination sites on the metal center that are necessary for the catalysis; that is, the catalytically active species does not contain phosphorus donor ligands coordinated to the

Table 1. Allylic Alkylation of Substrates 5 and 6 with $NaCH(CO_2Me)_2$[a]

entry	substrate	[Os]	*t* (h)	yield[b] (%)	ratio[b] **7**:**8**
1	**5a**	**1**	2	92	92:8
2	**5a**	**2**	6	88	96:4
			23	98	96:4
3	**5a**	**3**	6	64	94:6
			23	98	97:3
4	**5a**	**4**	5	19	96:4
			20	99	96:4
5	**5b**	**1**	7	54	90:10
			24	95	90:10
6	**5b**	**2**	7	35	94:6
			24	93	94:6
7	**5b**	**3**	7	22	96:4
			24	64	96:4
8	**5b**	**4**	6	30	87:13
			24	99	87:13
9	**6a**	**1**	24	57	83:17
10	**6a**	**2**	24	17	67:33
11	**6a**	**3**	24	4	67:33
12	**6a**	**4**	24	15	75:25
13	**6b**	**1**	21	14	83:17
14	**6b**	**4**	48	20	87:13

[a] See the Experimental Section for catalytic conditions. [b] Overall yields and ratios **7**:**8** were determined by ^{1}H NMR.

osmium atoms. In agreement with this, we have also observed that a racemic mixture of **7** is obtained from the alkylations of **5a** and **5b** in the presence of the chiral precursor **3**.

The catalysis has a marked dependence on the leaving group and the branched or linear nature of the substrates, in agreement with previous studies.[24c,25c,h,30] Thus, the alkylation of the carbonates **5a** and **6a** is easier than that of the acetates **5b** and **6b**. The alkylation of the branched substrates **5a** and **5b** is also easier than that of the linear isomers **6a** and **6b**. The branched product is the preferred one in all the cases, with branched:linear molar ratios between 87:13 and 97:3 for the alkylation of branched substrates and between 67:33 and 87:13 for the alkylation of the linear substrates.

The preferred formation of **7** from both **5b** and **6b** should be noted, which is in contrast with the $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2/PPh_3$-catalyzed regioselective allylic alkylation of monosubstituted allyl acetates with $[MeC(CO_2Me)_2]^-$, where the selective substitution at the position of the leaving group takes place.[33]

3. Reactions of 1 with 5a and with Sodium Dimethylmalonate. In order to obtain information about the active species for the catalysis, we have investigated the individual reactions between the components of the catalytic process corresponding to entry 1, i.e., the reactions of the dimer **1** with both 1-phenylallyl methylcarbonate and sodium dimethylmalonate.

Treatment in an NMR tube of a tetrahydrofuran-d_8 solution of **1** with 7.0 equiv of **5a** affords after 15 h at 60 °C a mixture of the organometallic species **1**, $\{OsCl(\eta^6\text{-}p\text{-cymene})\}_2(\mu\text{-OMe})_2$ (**9**), and $[\{Os(\eta^6\text{-}p\text{-cymene})\}_2(\mu\text{-OMe})_3][O_2COMe]$ (**10**) in a 5:8:2 molar ratio. The mixture is a result of the reactions shown in Scheme 3. In addition to cinnamyl chloride, methyl 1-phenylallyl ether and cinnamyl methylcarbonate are also detected as organic products. When the reaction is performed at preparatory scale in a Schlenk tube, the main organometallic species, complex **9**, is separated from the mixture as yellow crystals in 27% yield, by crystallization of the reaction crude in tetrahydrofuran/pentane.

Figure 2 shows a view of the structure of **9**. The molecule can be described as a symmetrical dimer formed by $OsCl(\eta^6$-

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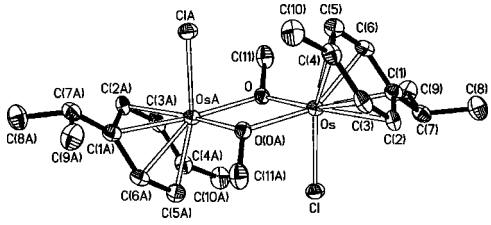

Figure 2. Molecular diagram of complex **9**. Selected bond lengths (Å) and angles (deg): Os−O 2.101(3), Os−O(0A) 2.123(4), Os−Cl 2.4162(13); O−Os−O(0A) 74.12(16), O−Os−Cl 82.68(10), O(0A)−Os-Cl 85.16(10).

p-cymene) moieties, which are joined by two bridging methoxy groups. The Os_2O_2 core forms a rhomb with Os−O distances of 2.101(3) and 2.123(4) Å, and O−Os−O and Os−O−Os angles of 74.12(16)° and 105.88(16)°, respectively. The geometry around each osmium is close to octahedral, with the arene occupying three sites of a face. The angles O−Os−Cl and O(OA)−Os-Cl are 82.68(10)° and 85.16(10)°, respectively. In agreement with the presence of the bridging methoxy ligands in the molecule, the ^{1}H and ^{13}C{^{1}H} NMR spectra show singlets at 4.15 and 69.3 ppm, respectively.

The formation of **9** can be rationalized according to Scheme 4. In solution, the coordinatively saturated dimer **1** is in equilibrium with the 16-valence-electron monomer $OsCl_2(\eta^6$-*p*-cymene) (**a**). The coordination of the C−C double bond of the substrate to the metal center of this species and the subsequent dissociation of chloride from the resulting saturated intermediate **b** could lead to **c**. The oxidative addition of the O−C bond of the substrate to the metal center of the latter should give the allyl derivative **d**, which could undergo nucleophilic attack of the dissociated chloride on the terminal CH_2 group of its allyl ligand, to afford **e** and cinnamyl chloride. The deinsertion of carbon dioxide and the association of **f** should generate **9**.

Complex **9** is certainly an intermediate stage in the path toward **10**. In agreement with this, we have also observed that the addition of 50 equiv of **5a** to a tetrahydrofuran-d_8 solution of **9** in an NMR tube leads to **10** and cinnamyl chloride in quantitative yield. After 18 h at 60 °C, about 75% of the substrate is transformed into cinnamyl methylcarbonate (about 55%) and methyl 1-phenylallyl ether (about 20%). The presence of **10** in the mixture is supported by the ^{1}H and ^{13}C{^{1}H} NMR spectra. In accordance with the previously reported salt [{$Os(\eta^6$-*p*-cymene)}$_2(\mu$-OMe)$_3$]PF_6,[34] the ^{1}H NMR spectrum contains a singlet at 4.57 ppm due to the bridging methoxy ligands. The carbonate anion displays a singlet at 3.30 ppm. In the ^{13}C{^{1}H} NMR spectrum, the signal due to the methoxy ligand appears as a singlet at 69.1 ppm, while two singlets at 49.7 and 167.5 ppm are characteristic of the anion.

The formation of **10** can be rationalized through a similar process to the formation of **9**, starting from the 16-valence-electron intermediate **f** (Scheme 5). The coordination of the C−C double bond of the substrate to the metal center of **f** followed by the dissociation of chloride should give **h**, related to **c** but containing a methoxy group instead of a chloride ligand. The oxidative addition of the O−C bond of the substrate to the metal center of the unsaturated **h** could afford **i**, which should lead to **j** and cinnamyl chloride by attack of the dissociated chloride to the CH_2 group of the allyl ligand. The loss of carbon dioxide from **j** could give **k**. The displacement of the methylcarbonate ligand of **j** by the fragment **k** should finally generate **10**.

The observed isomerization of the substrate and the formation of methyl 1-phenylallyl ether is consistent with the dissociation of the methylcarbonate and methoxy groups from the metal center. Thus, the formation of these organic products can be rationalized as a result of the addition of the nucleophiles present in the reaction mixture to allyl intermediates related to **d** and **i**.

Complexes **1** and **9** react with sodium dimethylmalonate. Treatment at 60 °C of tetrahydrofuran solutions of both compounds with 4.0 equiv of the nucleophile leads after 3−4 h to the formation of the bis(dimethylmalonate) derivate Os{κ^1-C^3-[$CH(CO_2Me)_2$]}{κ^2-*O,O*-[$CH(CO_2Me)_2$]}(η^6-*p*-cymene) (**11**), containing two dimethylmalonate ligands coordinated in different fashion. One of them is bonded to the metal center by the central C^3-carbon atom, while the other one acts as a chelate ligand through the oxygen atoms of the carbonyl groups. Complex **11** is isolated as yellow crystals in 53% yield, according to Scheme 6.

Figure 3 shows a view of the structure of **11**, which proves the different coordination of the dimethylmalonate ligands. The geometry around the osmium atom is close to octahedral, with the arene occupying three sites of a face. The chelate dimethylmalonate group acts with a bite angle O(5)−Os−O(7) of 85.27(11)°, whereas the angles O(7)−Os−C(1) and O(5)−Os−C(1) are 82.93(4)° and 84.06(13)°, respectively. The Os−C(1) bond length of 2.200(4) Å, which is about 0.03 Å shorter than that found in the related bis(acetylacetonate) derivative Os{κ^1-C^3-[$CH(COMe)_2$]}{κ^2-*O,O*-[$CH(COMe)_2$]}(η^6-1,2-$C_6H_4Me_2$) (2.233(4) Å),[35] lies within the range reported for the limited number of Os−C(sp^3) complexes characterized by X-ray diffraction analysis (2.15−2.21) Å.[36]

The structural parameters of each dimethylmalonate group reveal their different nature. In agreement with an sp^3-hybridization at C(1), the angles around this atom are between 106.5(3)° and 113.8(4)°, while the angles around the central carbon atom of the chelate counterpart, between 119.1(4)° and 121.9(4)°, support an sp^2-hybridization at C(8). As a consequence of the different hybridization at each central carbon atom, the separations between them and the corresponding carbonyl groups are also significantly different, 1.490(6) (C(1)−C(2)) and 1.477(6) (C(1)−C(4)) Å versus 1.402(6) (C(6)−C(8)) and 1.380(6) (C(8)−C(9)) Å. As expected the O−C bond lengths are also significantly different: 1.205(5) (O(1)−C(2)) and (O(3)−C(4)) Å versus 1.262(5) (O(5)−C(6)) and 1.264(5) (O(7)−C(9)) Å.

The IR and the ^{1}H and ^{13}C{^{1}H} NMR spectra are consistent with the structure shown in Figure 3 and with the presence in the molecule of two dimethylmalonate groups coordinated in different fashion. Thus, the IR in KBr shows two pairs of strong ν(CO) bands, one of them due to the chelate ligand at ca. 1505 and 1430 cm^{-1} and the other one at 1732 and 1617 cm^{-1} assignable to the monodentate group. The ^{1}H NMR spectrum contains singlets at 3.59 and 4.16 ppm, due to the methyl and CH protons, respectively, of the chelate ligand and at 3.42 and 3.71 ppm corresponding to the methyl and Os-CH protons of

(34) Cabeza, J.; Mann, B. E.; Maitlis, P. M.; Brevard, C. *J. Chem. Soc., Dalton Trans.* **1988**, 629.

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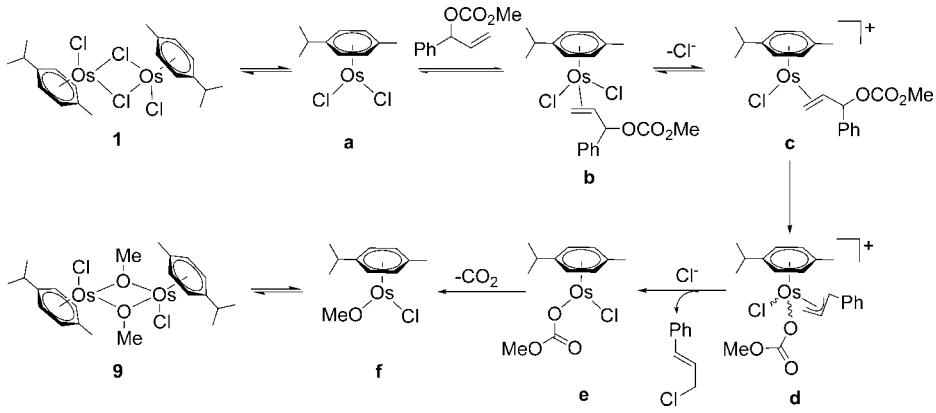
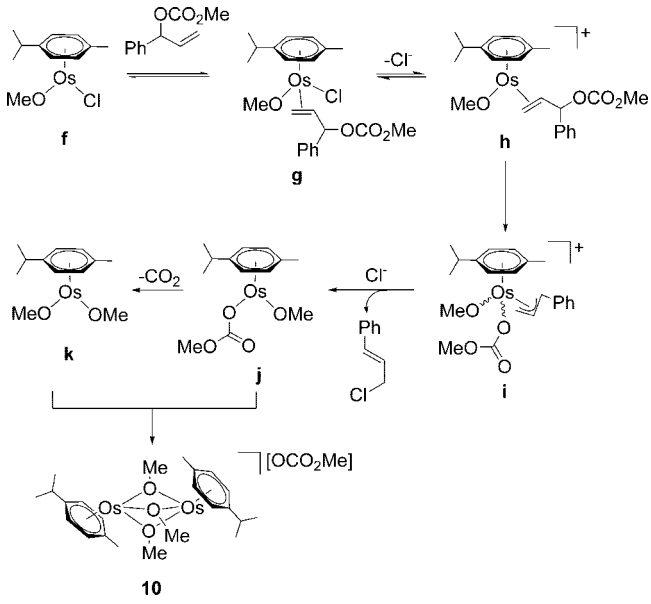
(36) (a) Lindner, E.; Jansen, R.-M.; Hiller, W.; Fawzi, R. *Chem. Ber.* **1989**, *122*, 1403. (b) Kiel, W. A.; Ball, R. G.; Graham, W. A. G. *J. Organomet. Chem.* **1990**, *383*, 481. (c) Esteruelas, M. A.; Lahoz, F. J.; López, J. A.; Oro, L. A.; Schlünken, C.; Valero, C.; Werner, H. *Organometallics* **1992**, *11*, 2034. (d) Bellachioma, G.; Cardaci, G.; Macchioni, A.; Zanazzi, P. *Inorg. Chem.* **1993**, *32*, 547. (e) Esteruelas, M. A.; González, A. I.; López, A. M.; Oñate, E. *Organometallics* **2003**, *22*, 414. (f) Esteruelas, M. A.; López, A. M.; Oñate, E.; Royo, E. *Organometallics* **2005**, *24*, 5780.

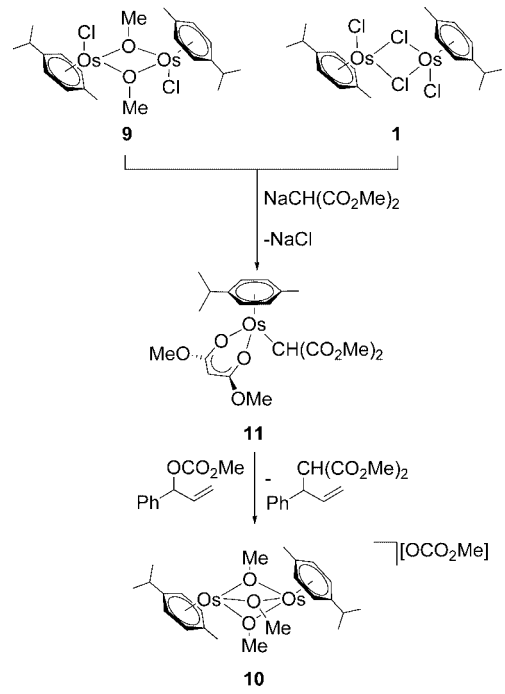
Scheme 4



Scheme 5



Scheme 6



the monodentate group. In the $^{13}C\{^1H\}$ NMR spectrum, the chelate ligand displays singlets at 52.1 (CH_3), 67.7 (CH), and 174.9 (CO) ppm, whereas the counterpart resonances of the monodentate group appear at 32.1 (CH), 50.1 (CH_3), and 174.5 (CO) ppm.

Under catalytic conditions **11** affords **10** at slower rates than those starting from **1** and **9**. In agreement with this, we have observed that the treatment at 60 °C of tetrahydrofuran solutions of **11** with 6.0 equiv of **5a** leads after 96 h to **10**, in addition to **7** as organic product (Scheme 6). By this procedure, complex **10** is obtained as a brown solid in 36% yield. The presence of the methylcarbonate anion in the salt is supported by the IR of the solid, which contains ν(CO) bands at 1728 and 1591 cm^{-1}.

4. The Active Species and Some Comments about the Mechanism of the Catalysis. The alkylation of **5a** with sodium dimethylmalonate in the presence of **9**, **10**, and **11** has been also investigated. Figure 4 shows the percentage of formed **7** as a function of time.

Dimers **9** and **10** are active precursors. The activity of both compounds is the same as that of **1**. Because **10** is formed via **9** by reaction of **1** with the substrate and is the main organometallic compound in the presence of an excess of substrate (Scheme 3), it is reasonable to think that **10** is the responsible species for the catalysis in the three cases. This is consistent with the fact that the monomer **11**, which reacts slowly with **5a** to give **10** (Scheme 6), shows a long activation period and its activity does not reach that of the dimer precursors.

The osmium atoms of **10** are 18-valence-electron centers. The coordinatively saturated character of the complex prevents the access of the substrate to the metal centers and therefore the catalysis. The activation of **10**, which could occur by rupture of the triple methoxy bridge promoted by the methylcarbonate anion to form **j** and **k** (Schemes 5 and 7), is therefore necessary. The coordination of the substrate to these unsaturated species should give **m** and **l**, which would afford the catalytic intermediate **h** by dissociation of the methylcarbonate ligand and a methoxy group, respectively. In agreement with Scheme 5, the oxidative addition of the O−C bond of the coordinated substrate to the metal center of **h** should afford the allyl intermediate **i**. The proposed structure for this intermediate with coordination *endo* of the allyl group is the preferred form in d^4-M(η^5-C_5H_5)L_2(η^3-allyl) derivatives (L ≠ CO), including osmium complexes.[37] The attack of the nucleophile to the CHPh-carbon atom of the allyl ligand of **i** should finally lead to **7**.

As it has been previously mentioned, osmium shows preference to coordination saturation. According to this, the rate-determining step of the catalysis should be the dissociation of the methylcarbonate group of the intermediate **m**, while the oxidative addition of the O−C bond of the substrate and the

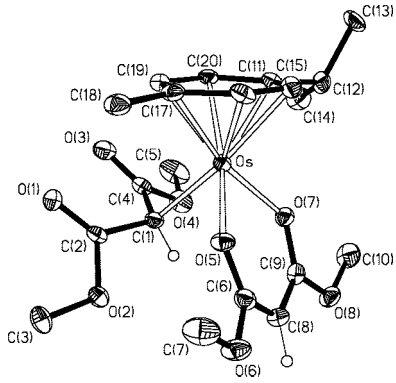


Figure 3. Molecular diagram of complex **11**. Selected bond lengths (Å) and angles (deg): Os−O(7) 2.098(3), Os−O(5) 2.103(3), Os−C(1) 2.200(4), O(1)−C(2) and O(3)−C(4) 1.205(5), O(5)−C(6) 1.262(5), O(7)−C(9) 1.264(5); O(5)−Os-O(7) 85.27(11), O(7)−Os-C(1) 82.93(14), O(5)−Os-C(1) 84.06(13), C(2)−C(1)−C(4) 113.8(4), C(4)−C(1)−Os 106.5(3), C(2)−C(1)−Os 110.7(3), C(4)−C(1)−H(1) 108(3), C(2)−C(1)−H(1) 110(3), Os−C(1)-H(1) 108(3), C(9)−C(8)−C(6) 121.9(4), C(9)−C(8)−H(8) 119.1, C(6)−C(8)−H(8) 119.1.

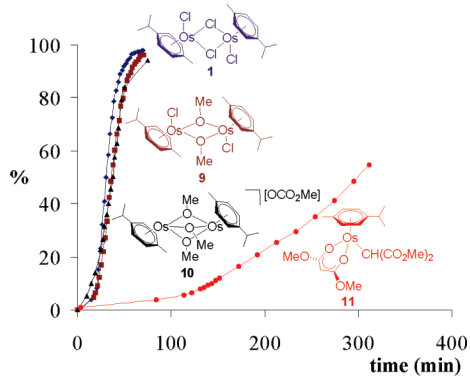
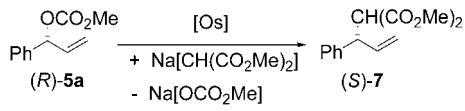


Figure 4. Formation of **7** as a function of the time using **1**, **9**, **10**, and **11** as catalyst precursors.

attack of the nucleophile to the allyl ligand should be fast steps. The oxidative addition is favored by the osmium trend to stabilize redox isomers with more metal−carbon bonds. In favor of a rapid attack of the nucleophile to the allyl ligand (before any isomerization process), we have observed that in the presence of **1** the allylic alkylation of an enantiomerically enriched substrate (*R*)-**5a** (93% ee) with sodium dimethylmalonate yields (95%) an enantiomerically enriched product (*S*)-**7** (83% ee), according to eq 2. A similar effect has been observed with other systems.[22,23a,24a,c,30]



(2)

5. Activation of $OsCl_2(\eta^6$-*p*-cymene)L. In contrast to **1**, the mononuclear phosphoramidite complexes **2** and **3** do not react with **5a** in the absence of sodium dimethylmalonate. Thus, the ^1H NMR spectra of these compounds in tetrahydrofuran-d_8 at 60 °C do not show significant changes after the addition of 25 equiv of substrate. However, the treatment at room temperature of tetrahydrofuran solutions of both compounds with 4.0 equiv of sodium dimethylmalonate produces the replacement of one of the chloride ligands by a dimethylmalonate group to afford the chloro-dimethylmalonate derivatives $Os\{\kappa^1$-C^3-$[CH(CO_2Me)_2]\}Cl(\eta^6$-*p*-cymene)L (L = L^1 (**12**), L^2 (**13**)), which contain the dimethylmalonate ligand coordinated to the metal center through the central C^3-carbon atom. Complexes **12** and **13** are isolated as dark yellow solids in 68% and 63% yield, respectively, according to Scheme 8.

Figure 5 shows a view of the structure of **12**. The geometry around the osmium atom is close to octahedral, with the arene occupying three sites of a face. The angles C(1)−Os−P, C(1)−Os−Cl, and P−Os−Cl are 90.19(15)°, 84.62(16)°, and 84.21(5)°, respectively. The Os−C(1) bond length of 2.242(6) Å is similar to the counterpart distance in **11**. The structural parameters within the dimethylmalonate group also agree well with those of the κ^1-C^3-dimethylmalonate of **11**. Thus, the angles around C(1) are between 107(4)° and 113(4)°. The separations between C(1) and the carbonyl groups are 1.477(8) (C(1)−C(4)) and 1.485(8) (C(1)−C(2)) Å, whereas the C(2)−O(2) and C(4)−O(4) distances are 1.208(7) and 1.221(7) Å, respectively.

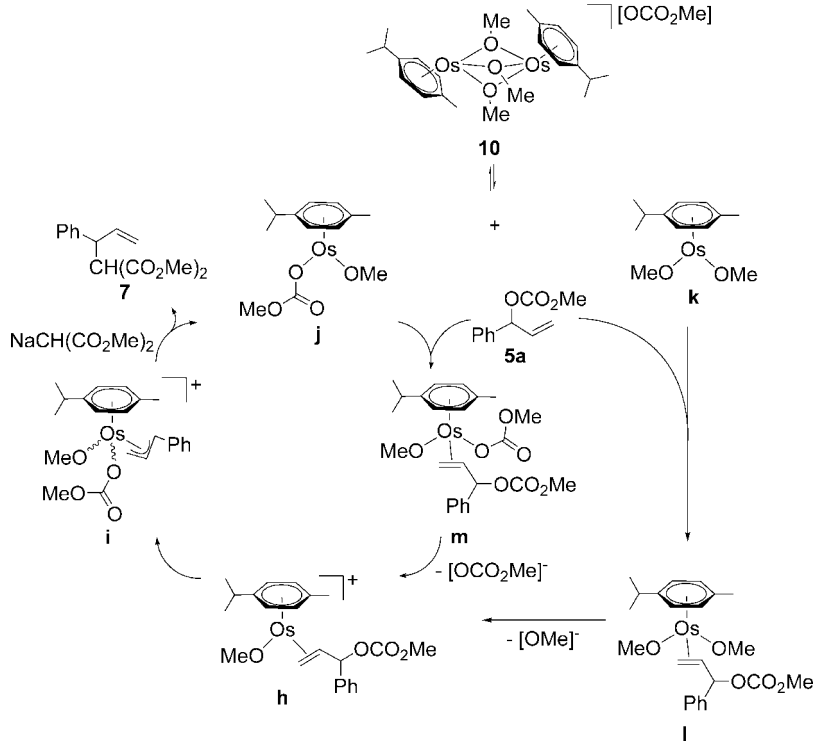
The IR and the ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of **12** and **13** are consistent with the structure shown in Figure 5. In agreement with the presence of a κ^1-C^3-dimethylmalonate ligand in the molecules, the IR of both compounds contains two ν(CO) bands at 1718 and 1619 (**12**) cm^{-1} and at 1732 and 1619 (**13**) cm^{-1}. In the ^1H NMR spectrum of **12** the OsCH resonance of the dimethylmalonate group appears at 5.06 ppm as a doublet with a H−P coupling constant of 6.9 Hz. The most noticeable resonance of the phosphoramidite ligand is a doublet at 2.76 ppm with a H−P coupling constant of 9.2 Hz due to the methyl groups. In the $^{13}C\{^1H\}$ NMR spectrum the OsC resonance appears at 18.9 ppm as a doublet with a C−P coupling constant of 9.4 Hz. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 102.5 ppm. The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of **13** reveal that in solution this compound exists as a 7:3 mixture of two diastereomers, which are a consequence of the chirality of both the metal center and the phosphorus donor ligand. In the ^1H NMR spectrum, the most noticeable resonances of the major isomer are two doublets at 2.89 and 4.94 ppm with H−P coupling constants of 8.4 and 7.6 Hz due to the methyl groups of the phosphoramidite and to the OsCH proton of the dimethylmalonate. A doublet at 17.4 ppm with a C−P coupling constant of 20.1 Hz, corresponding to the OsC carbon in the $^{13}C\{^1H\}$ NMR spectrum, and a singlet at 106.3 ppm in the $^{31}P\{^1H\}$ NMR spectrum are also characteristic of this isomer.

Complexes **12** and **13** show a similar behavior to **2** and **3** toward **5a** and sodium dimethylmalonate. None of these compounds react with the substrate in the absence of the nucleophile. However, the treatment of their tetrahydrofuran solutions with an excess of sodium dimethylmalonate produces the replacement of the chloride and phosphoramidite ligands by a chelate dimethylmalonate group, to afford the bis(dimethylmalonate) **11** (Scheme 8).

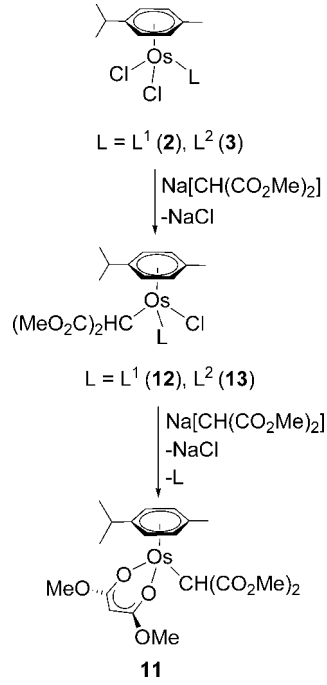
The catalytic activities of **12** and **13** are the same as those of the corresponding dichloro derivatives **2** and **3**. Figure 6 shows the percentage of formed **7** as a function of time, in the presence of **3** and **13**. Since complex **11** reacts with the substrate to give **10** (Scheme 6), at first glance, one could think that the activation of **2** and **3** would take place by means of the formation of **10**, through the reactions shown in Scheme 8. However, it should be noted that, according to Figure 6, the activities of these phosphoramidite complexes are intermediate between those of **10** and **11**. So, this possibility must be rejected.

(37) Esteruelas, M. A.; González, A. I.; López, A. M.; Oliván, M.; Oñate, E. *Organometallics* **2006**, *25*, 693, and references therein.

Scheme 7



Scheme 8



In order to find an explanation for the catalytic activity of the phorphoramidite precursors, we carried out a careful revision of the ^{1}H NMR spectra of the reaction mixture using **13** as catalytic precursor. Figure 7 clearly shows that the alkylation products **7** and **8** start to be formed when the methyl resonance of the phosphoramidite ligand disappears. This suggests that the activation of **2**, **3**, **12**, and **13** is a consequence of the decomposition of the phosphorus donor ligand. The fact that the activities of these compounds do not reach that of **10** may be due to the poisoning of the active species with the side products of the destruction of the phosphoramidites.

Concluding Remarks

This study has revealed that from the metals in the iron triad not only iron and ruthenium but also osmium forms complexes that behave as good catalytic precursors for the allylic alkylation. Starting from both branched and linear substrates, branched-type products are preferentially formed with branched:linear molar ratios between 97:3 and 67:33 depending upon the substrate and the ligands of the catalytic precursor.

A mechanistic study on the alkylation of 1-phenylallyl methylcarbonate with sodium dimethylmalonate in the presence of the dimer $[OsCl_2(\eta^6\text{-}p\text{-cymene})]_2$ proves that the precursor is activated by means of the reaction with the substrate to afford $[\{Os(\eta^6\text{-}p\text{-cymene})\}_2(\mu\text{-OMe})_3][O_2COMe]$ via $\{OsCl(\eta^6\text{-}p\text{-cymene})\}_2(\mu\text{-OMe})_2$.

The coordination of phosphoramidite ligands to the metal centers of $[OsCl_2(\eta^6\text{-}p\text{-cymene})]_2$, to give $OsCl_2(\eta^6\text{-}p\text{-cymene})L$, inhibits the reaction with the substrate, reducing the efficiency of the precursor. In these cases the catalysis starts after the

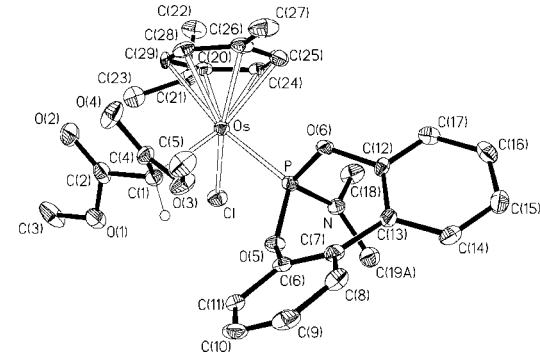


Figure 5. Molecular diagram of complex **12**. Selected bond lengths (Å) and angles (deg): Os−P 2.2940(15), Os−Cl 2.4111(14), Os−C(1) 2.242(6), C(1)−C(2) 1.485(8), C(1)−C(4) 1.477(8), C(2)−O(2) 1.208(7), C(4)−O(4) 1.221(7), C(1)−Os−P 90.19(15), C(1)−Os−Cl 84.62(16), P−Os−Cl 84.21(5).

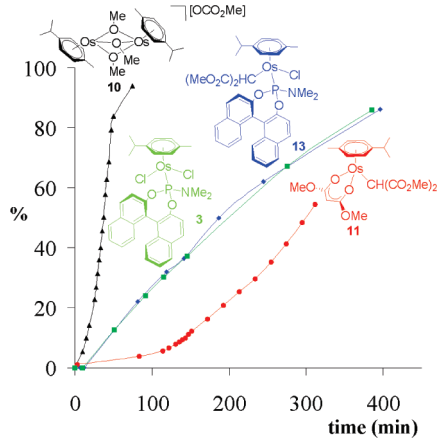


Figure 6. Formation of **7** as a function of the time using **3**, **10**, **11**, and **13** as catalyst precursors.

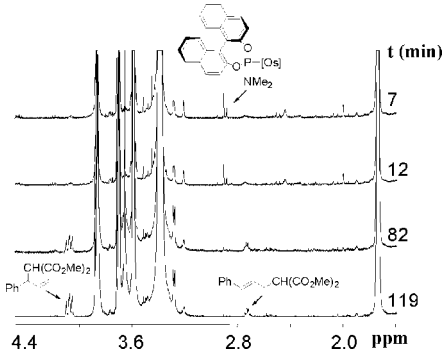


Figure 7. Selected ^{1}H NMR spectra of the alkylation of **5a** in the presence of **13** (THF-d_8).

phosphorus-donor ligand decomposition. This process also occurs on Os{κ^1-C^3-[CH(CO$_2$Me)$_2$]}Cl(η^6-*p*-cymene)L species, containing a dimethylmalonate ligand coordinated to the metal center through the central C^3-carbon atom.

In conclusion, we report the first osmium-based allylic alkylation catalysts and a mechanistic study of one of these reactions.

Experimental Section

All reactions were carried out under argon using standard Schlenk tube techniques. THF, dichloromethane, pentane, and toluene were obtained oxygen- and water-free from an MBraun solvent purification apparatus. Other solvents were dried and purified by known procedures and distilled under argon prior to use. IR spectra were recorded with a Spectrum One spectrometer as neat solids or KBr pellets. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded with a Varian Gemini 2000-300 MHz, a Bruker Avance 300, or a Bruker ARX Avance 400 spectrometer. Chemical shifts are referenced to residual solvent peaks (^{1}H, ^{13}C{^{1}H}) or external H_3PO_4 (85%) (^{31}P{^{1}H}). Coupling constants are given in hertz. C, H, and N analyses were performed with a Perkin-Elmer 2400 CHNS/O analyzer. Substrates and products of catalysis either are commercially available or have been previously described in the literature.[38] The phosphoramidite ligands used in this paper[30,31] and complexes [OsCl$_2$(η^6-*p*-cymene)]$_2$ (**1**),[11] [{Os$_2$(η^6-*p*-cymene)$_2$}(μ-OMe)$_3$][PF$_6$],[34] and OsCl$_2$(η^6-*p*-cymene){P(OPh)$_3$} (**4**)[32] were prepared according to the literature.

Synthesis of OsCl$_2$(η^6-*p*-cymene)L^1 (2). A solution of L^1 (162 mg, 0.63 mmol) in toluene (5 mL) was added to a stirred suspension of [OsCl$_2$(η^6-*p*-cymene)]$_2$ (**1**; 250 mg, 0.32 mmol) in toluene (5 mL). The mixture was stirred for 18 h and then filtered, and the orange precipitate washed with pentane (16 mL). Crystallization of the crude mixture from dichloromethane/diethyl ether gave **2** as orange crystals (319 mg, 0.49 mmol, 77% yield). ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 298 K): δ 1.16 [d, J_{HH} = 6.9 Hz, 6 H, (*CH*$_3$)$_2$CH, *p*-cymene], 2.13 (s, 3 H, C*H*$_3$, *p*-cymene), 2.75 [sept, J_{HH} = 6.9 Hz, 1 H, (CH$_3$)$_2$C*H*, *p*-cymene], 2.79 [d, J_{HP} = 9.9 Hz, 6 H, N(*CH*$_3$)$_2$], 5.31 (d, J_{HH} = 5.7 Hz, 2 H, C*H*-*arom*, *p*-cymene), 5.53 (d, J_{HH} = 5.7 Hz, 2 H, C*H*-*arom*, *p*-cymene), 7.35−7.45 (m, 6 H, C*H*-*arom*, L^1), 7.50−7.55 (m, 2 H, C*H*-*arom*, L^1). ^{13}C{^{1}H} NMR (75.45 MHz, CD$_2$Cl$_2$, 298 K): δ 17.6 (s, *C*H$_3$, *p*-cymene), 21.9 [s, (*C*H$_3$)$_2$CH, *p*-cymene], 30.1 [s, (CH$_3$)$_2$*C*H, *p*-cymene], 37.6 [d, J_{CP} = 4.5 Hz, N(*C*H$_3$)$_2$], 80.5 (d, J_{CP} = 6.2 Hz, *C*H-*arom*, *p*-cymene), 82.6 (d, J_{CP} = 4.7 Hz, *C*H-*arom*, *p*-cymene), 97.3 (d, J_{CP} = 2.9 Hz, CH$_3$*C*$_{ipso}$, *p*-cymene), 101.5 [d, J_{CP} = 2.7 Hz, (CH$_3$)$_2$CH*C*$_{ipso}$, *p*-cymene], 122.7 (d, J_{CP} = 3.5 Hz, *C*H-*arom*, L^1), 125.5 (s, *C*H-*arom*, L^1), 129.3, 130.0 (both s, *C*H-*arom*, L^1), 130.1 (d, J_{CP} = 1.8 Hz, *C*$_{ipso}$-*arom*, L^1), 150.2 (d, J_{CP} = 9.7 Hz, *C*$_{ipso}$, *C*OP-L^1). ^{31}P{^{1}H} NMR (121.48 MHz, CD$_2$Cl$_2$, 298 K): δ 121.5. Anal. Calcd for C$_{24}$H$_{28}$Cl$_2$NO$_2$OsP: C, 44.00; H, 4.31; N, 2.14. Found: C, 44.20; H, 4.37; N, 2.23.

Synthesis of OsCl$_2$(η^6-*p*-cymene)L^2 (3). A solution of L^2 (226 mg, 0.63 mmol) in toluene (5 mL) was added to a stirred suspension of [OsCl$_2$(*p*-cymene)]$_2$ (**1**; 250 mg, 0.32 mmol) in toluene (5 mL) and the mixture stirred for 18 h at rt. Then, it was filtered and the orange precipitate washed with pentane (16 mL) and recrystallized from a dichloromethane/diethyl ether mixture (380 mg, 0.50 mmol, 52% yield). ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 298 K): δ 1.13 [d, J_{HH} = 6.9 Hz, 3 H, (*CH*$_3$)$_2$CH, *p*-cymene], 1.15 [d, J_{HH} = 6.9 Hz, 3 H, (*CH*$_3$)$_2$CH, *p*-cymene], 2.18 (s, 3 H, C*H*$_3$, *p*-cymene), 2.70 [d, J_{HP} = 10.2 Hz, 6 H, N(*CH*$_3$)$_2$], 2.80 [sept, J_{HH} = 6.9 Hz, 1 H, (CH$_3$)$_2$C*H*, *p*-cymene], 5.10 (d, J_{HH} = 5.5 Hz, 1 H, C*H*-*arom*, *p*-cymene), 5.46 (d, J_{HH} = 5.8 Hz, 1 H, C*H*-*arom*, *p*-cymene), 5.52 (d, J_{HH} = 5.5 Hz, 1 H, C*H*-*arom*, *p*-cymene), 5.66 (d, J_{HH} = 5.8 Hz, 1 H, C*H*-*arom*, *p*-cymene), 7.28−7.37 (4 H, C*H*-*arom*, L^2), 7.48−7.55 (3 H, C*H*-*arom*, L^2), 7.93−8.18 (5 H, C*H*-*arom*, L^2). ^{13}C{^{1}H} NMR (75.45 MHz, CD$_2$Cl$_2$, 298 K): δ 17.8 (s, *C*H$_3$, *p*-cymene), 22.1 [d, J_{CP} = 5.9 Hz, N(*C*H$_3$)$_2$], 30.2 [s, (CH$_3$)$_2$*C*H, *p*-cymene], 37.6, 37.7 [both s, (*C*H$_3$)$_2$CH, *p*-cymene], 78.5 (d, J_{CP} = 3.7 Hz, *C*H-*arom*, *p*-cymene), 81.5 (d, J_{CP} = 4.7 Hz, *C*H-*arom*, *p*-cymene), 82.6 (d, J_{CP} = 8.0 Hz, *C*H-*arom*, *p*-cymene), 84.2 (d, J_{CP} = 4.5 Hz, *C*H-*arom*, *p*-cymene), 97.9 (d, J_{CP} = 2.8 Hz, CH$_3$*C*$_{ipso}$, *p*-cymene), 102.2 [d, J_{CP} = 2.9 Hz, (CH$_3$)$_2$CH*C*$_{ipso}$, *p*-cymene], 120.8 (d, J_{CP} = 1.8 Hz, *C*H-*arom*, L^2), 122.7 (d, J_{CP} = 2.3 Hz, *C*$_{ipso}$-*arom*, L^2), 123.1 (d, J_{CP} = 2.7 Hz, *C*$_{ipso}$-*arom*, L^2), 123.8 (d, J_{CP} = 3.2 Hz, *C*H-*arom*, L^2), 125.3, 125.4, 126.1, 126.5, 126.8, 126.9, 128.3, 128.4, 129.8, (all s, *C*H-*arom*, L^2), 130.6 (d, J_{CP} = 1.3 Hz, *CH*-*arom*, L^2), 131.4 (d, J_{CP} = 0.7 Hz, *C*$_{ipso}$-*arom*, L^2), 131.5 (d, J_{CP} = 1.1 Hz, *C*$_{ipso}$-*arom*, L^2), 132.6 (d, J_{CP} = 1.4 Hz, *C*$_{ipso}$-*arom*, L^2), 132.8 (d, J_{CP} = 1.8 Hz, *C*$_{ipso}$-*arom*, L^2), 148.3 (d, J_{CP} = 6.3 Hz, *C*$_{ipso}$, *C*OP- L^2), 149.7 (d, J_{CP} = 10.8 Hz, *C*$_{ipso}$, *C*OP-L^2). ^{31}P{^{1}H} NMR (121.48 MHz, CD$_2$Cl$_2$, 298 K): δ 108.3. Anal. Calcd for C$_{32}$H$_{32}$Cl$_2$NO$_2$OsP: C, 50.93; H, 4.27; N, 1.86. Found: C, 50.89; H, 4.31; N, 1.92.

Reaction of [OsCl$_2$(η^6-*p*-cymene)]$_2$ with CH$_2$CHCH(OCO$_2$Me)Ph: Formation of {OsCl(η^6-*p*-cymene)}$_2$(μ-OMe)$_2$ (9). A solution of [OsCl$_2$(η^6-*p*-cymene)]$_2$ (**1**; 200 mg, 0.25 mmol) in THF (6 mL) was treated with **5a** (389 mg, 2.01 mmol). After 24 h at 60 °C, the solvent was evaporated and the red oil obtained precipitated and washed with diethyl ether at −20 °C. The resultant yellow solid was finally washed with C$_6$H$_6$ (1 mL) and dried *in vacuo* (52 mg, 0.07 mmol, 27% yield). ^{1}H NMR (300 MHz, THF-d_8, 298

(38) (a) **5a**, **6a**, **6b**, and **7**: Lehmann, J.; Lloyd-Jones, G. C. *Tetrahedron* **1995**, *51*, 8863. Enantiomer analysis of **7** by HPLC: Chiracel ODH column, length: 4.6 × 250 mm, flow: 1 mL·min^{-1}, eluent: *n*-hexane/^{i}PrOH (98:2), t_R(*R*): 13.1 min, t_R(*S*): 13.9 min.

K): δ 1.25 [d, J_{HH} = 6.9 Hz, 6 H, (C*H*$_3$)$_2$CH, *p*-cymene], 2.24 (s, 3 H, C*H*$_3$, *p*-cymene), 2.77 [m, 1 H, (CH$_3$)$_2$C*H*, *p*-cymene], 4.15 (s, 3 H, OC*H*$_3$), 5.76 (s, 4 H, C*H*-*arom*, *p*-cymene). ^{13}C{^{1}H} NMR (75.47 MHz, THF-d_8, 298 K): δ 19.2 (s, *C*H$_3$, *p*-cymene), 23.1 [s, (*C*H$_3$)$_2$CH, *p*-cymene], 32.8 [s, (CH$_3$)$_2$*C*H, *p*-cymene], 69.3 (s, O*C*H$_3$), 70.6 (s, *C*H-*arom*, *p*-cymene), 72.1 (s, *C*H-*arom*, *p*-cymene), 84.9 (s, CH$_3$*C*$_{ipso}$, *p*-cymene), 87.2 [s, (CH$_3$)$_2$CH*C*$_{ipso}$, *p*-cymene]. Anal. Calcd for $C_{22}H_{34}Cl_2O_2Os_2$: C, 33.80; H, 4.38. Found: C, 33.75; H, 4.43.

Reaction of {OsCl(η^6-*p*-cymene)}$_2$(μ-OMe)$_2$ with CH$_2$CHCH(OCO$_2$Me)Ph: Formation of [{Os(η^6-*p*-cymene)}$_2$(μ-OMe)$_3$][OCO$_2$Me] (10). A solution of {OsCl(η^6-*p*-cymene)}$_2$(μ-OMe)$_2$ (**9**; 0.98 mg, 1.3 $\times$ 10^{-3} mmol) in THF-d_8 (0.5 mL) was treated with **5a** (12.5 mg, 0.065 mmol). After 18 h at 60 °C, the NMR spectrum of the mixture showed the quantitative transformation of complex **9** into **10** and cinnamyl chloride. Spectroscopic data for complex **10**. ^{1}H NMR (400 MHz, THF-d_8, 298 K): δ 1.27 [d, J_{HH} = 8.8 Hz, 12 H, (C*H*$_3$)$_2$CH, *p*-cymene], 2.25 (s, 6 H, C*H*$_3$, *p*-cymene), 2.66 [m, 2 H, (CH$_3$)$_2$C*H*, *p*-cymene], 3.30 (s, 3 H, OCO$_2$C*H*$_3$), 4.57 (s, 9 H, OC*H*$_3$), 5.94 (d, J_{HH} = 3.3 Hz, 4 H, *CH*-*arom*, *p*-cymene), 6.09 (d, J_{HH} = 3.3 Hz, 4 H, *CH*-*arom*, *p*-cymene). ^{13}C{^{1}H} NMR (100.6 MHz, THF-d_8, 298 K): δ 19.4 (s, *C*H$_3$, *p*-cymene), 23.0 [s, (*C*H$_3$)$_2$CH, *p*-cymene], 33.0 [s, (CH$_3$)$_2$*C*H, *p*-cymene], 49.7 (s, OCO$_2$*C*H$_3$), 69.1 (s, O*C*H$_3$), 66.7, 68.5 (both s, *C*H-*arom*, *p*-cymene), 83.0 (s, CH$_3$*C*$_{ipso}$, *p*-cymene), 87.0 [s, (CH$_3$)$_2$CH*C*$_{ipso}$, *p*-cymene], 167.5 (s, O*C*O$_2$CH$_3$).

Reaction of [OsCl$_2$(η^6-*p*-cymene)]$_2$ with NaCH(CO$_2$Me)$_2$: Formation of Os{κ^1-*C*^{3}-[CH(CO$_2$Me)$_2$]}{κ^2-*O*,*O*-[CH(CO$_2$Me)$_2$]}(η^6-*p*-cymene) (11). A freshly prepared solution of sodium dimethylmalonate (1.01 mmol, 3 mL, 0.34 M in THF), obtained by dropwise addition of dimethylmalonate (1.01 mmol, 115 μL) to a suspension of sodium hydride (1.01 mmol, 24 mg) in THF (3 mL), was added to a stirred suspension of [OsCl$_2$(η^6-*p*-cymene)]$_2$ (**1**; 200 mg, 0.25 mmol) in THF (3 mL) and the mixture stirred at 60 °C for 3 h. The color of the solution changed from light yellow to dark green. After removing the solvent, the residue was purified by flash column chromatography under argon (activated aluminum oxide, grade V) with diethyl ether (20 mL) and tetrahydrofuran (20 mL) as eluents. The THF fraction was evaporated to dryness to give a yellow solid (157 mg, 0.27 mmol, 53% yield). ^{1}H NMR (400 MHz, THF-d_8, 298 K): δ 1.22 [d, J_{HH} = 6.8 Hz, 6 H, (C*H*$_3$)$_2$CH, *p*-cymene], 1.94 (s, 3 H, C*H*$_3$, *p*-cymene), 2.54 [sept, J_{HH} = 6.8 Hz, 1 H, (CH$_3$)C*H*, *p*-cymene], 3.42 [s, 6 H, η^1-CH(CO$_2$C*H*$_3$)$_2$], 3.59 [s, 6 H, η^2-(*O*,*O*)-CH(CO$_2$C*H*$_3$)$_2$], 3.71 [s, 1 H, η^1-C*H*(CO$_2$CH$_3$)$_2$], 4.16 [s, 1 H, η^2-(*O*,*O*)-C*H*(CO$_2$CH$_3$)$_2$], 5.75 [AB spin system, $\Delta\nu$ = 33.5 Hz, J_{AB} = 5.6 Hz, 4 H, *CH*-*arom*, *p*-cymene]. ^{13}C{^{1}H} NMR (100.56 MHz, THF-d_8, 298 K): 17.4 (s, *C*H$_3$, *p*-cymene), 22.7 [s, (*C*H$_3$)$_2$CH, *p*-cymene], 31.1 [s, (CH$_3$)$_2$*C*H, *p*-cymene], 32.1 [s, η^1-*C*H(CO$_2$CH$_3$)$_2$], 50.1 (s, η^1-CH(CO$_2$*C*H$_3$)$_2$], 52.1 (s, η^2-(*O*,*O*)-CH(CO$_2$*C*H$_3$)$_2$], 67.7 (s, η^2-(*O*,*O*)-*C*H(CO$_2$CH$_3$)$_2$], 74.0, 76.7 (both s, *C*H-*arom*, *p*-cymene), 82.4 (s, CH$_3$*C*$_{ipso}$, *p*-cymene), 89.8 [s, (CH$_3$)$_2$CH*C*$_{ipso}$, *p*-cymene], 174.5 [s, η^1-CH(*C*O$_2$CH$_3$)$_2$], 174.9 [s, η^2-(*O*,*O*)-CH(*C*O$_2$CH$_3$)$_2$]. IR (KBr, cm^{-1}): 1732, 1617, 1505, 1430 [ν_{CO}]. Anal. Calcd for $C_{20}H_{28}O_8Os$: C, 40.95; H, 4.21. Found: C, 40.49; H, 4.02.

Reaction of {OsCl(η^6-*p*-cymene)}$_2$(μ-OMe)$_2$ with NaCH(CO$_2$Me)$_2$: Formation of Os{κ^1-*C*^{3}-[CH(CO$_2$Me)$_2$]}{κ^2-*O*,*O*-[CH(CO$_2$Me)$_2$]}(η^6-*p*-cymene) (11). A solution of {OsCl(η^6-*p*-cymene)}$_2$(μ-OMe)$_2$ (**9**; 50 mg, 0.06 mmol) in THF (3 mL) was treated with a freshly prepared solution of Na[CH(CO$_2$Me)$_2$] (0.4 mmol, 3 mL, 0.13 M in THF) at 60 °C. The ^{1}H NMR spectrum of the reaction mixture after 4 h at 60 °C showed the presence of complex **11**.

Reaction of Os{κ^1-*C*^{3}-[CH(CO$_2$Me)$_2$]}{κ^2-*O*,*O*-[CH(CO$_2$Me)$_2$]}(η^6-*p*-cymene) with CH$_2$CHCH(OCO$_2$Me)Ph: Formation of [{Os(η^6-*p*-cymene)}$_2$(μ-OMe)$_3$][OCO$_2$Me] (10). A mixture of Os{κ^1-*C*^{3}-[CH(CO$_2$Me)$_2$]}{κ^2-*O*,*O*-[CH(CO$_2$Me)$_2$]}(η^6-*p*-cymene) (**11**; 200 mg, 0.34 mmol) and CH$_2$CHCH(OCO$_2$Me)Ph (**5a**; 393 mg, 2.04 mmol) in THF (8 mL) was stirred at 60 °C for 96 h. The solvent was then evaporated and the residue washed with diethyl ether at −20 °C to precipitate a brown solid, which was dried *in vacuo* (50 mg, 0.06 mmol, 36% yield). IR (neat compound, cm^{-1}): 1728, 1591 [ν_2CO)]. Anal. Calcd for $C_{25}H_{40}O_6Os_2$: C, 36.75; H, 4.93. Found: C, 36.94; H, 4.71.

Reaction of OsCl$_2$(η^6-*p*-cymene)L^1 with Na[CH(CO$_2$Me)$_2$]: Formation of Os{κ^1-*C*^{3}-[CH(CO$_2$Me)$_2$]}Cl(η^6-*p*-cymene)L^1 (12). A freshly prepared solution of sodium dimethylmalonate (5.01 mmol, 6 mL, 0.84 M in THF) was added to a stirred suspension of OsCl$_2$(η^6-*p*-cymene)L^1 (**2**; 820 mg, 1.25 mmol) in THF (4 mL) and the mixture stirred at rt for 3 h. After removing the solvent, the colored residue was purified by flash column chromatography under argon (activated aluminum oxide, grade V) with diethyl ether (20 mL) and THF (20 mL) as eluents. The THF fraction was evaporated to dryness and the complex precipitated with cold pentane and isolated by filtration as an orange solid (636.3 mg, 0.85 mmol, 68% yield). ^{1}H NMR (300 MHz, C$_6$D$_6$, 298 K): δ 0.96 [d, J_{HH} = 6.9 Hz, 3 H, (C*H*$_3$)$_2$CH, *p*-cymene], 2.02 [d, J_{HH} = 6.9 Hz, 3 H, (C*H*$_3$)$_2$CH, *p*-cymene], 1.98 (s, 3 H, C*H*$_3$, *p*-cymene), 2.52 [sept, J_{HH} = 6.9 Hz, 1 H, (CH$_3$)$_2$C*H*, *p*-cymene], 2.76 [d, J_{HP} = 9.2 Hz, 6 H, N(C*H*$_3$)$_2$], 3.29, 3.60 [both s, 3 H, CH(CO$_2$C*H*$_3$)$_2$], 4.94 (d, J_{HH} = 5.4 Hz, 1 H, C*H*-*arom*, *p*-cymene), 5.00 (d, J_{HH} = 5.4 Hz, 1 H, C*H*-*arom*, *p*-cymene), 5.06 [d, J_{HP} = 6.9 Hz, 1 H, C*H*(CO$_2$CH$_3$)$_2$], 5.53 (d, J_{HH} = 5.7 Hz, 1 H, C*H*-*arom*, *p*-cymene), 5.56 (d, J_{HH} = 5.7 Hz, 1 H, C*H*-*arom*, *p*-cymene), 7.20−7.86 (6 H, C*H*-*arom*, L^1), 7.19 (d, J_{HH} = 7.2 Hz, 1 H, C*H*-*arom*, L^1), 7.49 (d, J_{HH} = 7.8 Hz, 1 H, C*H*-*arom*, L^1). ^{13}C{^{1}H} NMR (75.45 MHz, C$_6$D$_6$, 298 K): δ 17.0 (s, *C*H$_3$, *p*-cymene), 18.9 [d, J_{CP} = 9.4 Hz, *C*H(CO$_2$CH$_3$)$_2$], 22.0, 22.6 [both s, (*C*H$_3$)$_2$CH, *p*-cymene], 30.4 [s, (CH$_3$)$_2$*C*H, *p*-cymene], 38.6 [d, J_{CP} = 3.9 Hz, N(*C*H$_3$)$_2$], 50.15, 50.2 [both s, CH(CO$_2$*C*H$_3$)$_2$], 75.7 (d, J_{CP} = 8.0 Hz, *C*H-*arom*, *p*-cymene), 80.4 (d, J_{CP} = 9.3 Hz, *C*H-*arom*, *p*-cymene), 85.6 (d, J_{CP} = 5.6 Hz, *C*H-*arom*, *p*-cymene), 85.7 (d, J_{CP} = 1.7 Hz, *C*H-*arom*, *p*-cymene), 94.6 (d, J_{CP} = 4.6 Hz, CH$_3$*C*$_{ipso}$ *p*-cymene), 110.4 [d, J_{CP} = 1.8 Hz, (CH$_3$)$_2$CH*C*$_{ipso}$ *p*-cymene], 122.5 (d, J_{CP} = 3.5 Hz, *C*H-*arom*, L^1), 124.1 (d, J_{CP} = 3.8 Hz, *C*H-*arom*, L^1), 125.1 (d, J_{CP} = 1.3 Hz, *C*H-*arom*, L^1), 125.4 (d, J_{CP} = 1.7 Hz, *C*H-*arom*, L^1), 129.4 (d, J_{CP} = 1.1 Hz, *C*H-*arom*, L^1), 129.6 (d, J_{CP} = 1.0 Hz, *C*H-*arom*, L^1), 129.7 (d, J_{CP} = 2.0 Hz, *C*$_{ipso}$-*arom*, L^1), 130.2 (d, J_{CP} = 1.6 Hz, *C*H-*arom*, L^1), 130.9 (d, J_{CP} = 1.2 Hz, *C*H-*arom*, L^1), 131.0 (d, J_{CP} = 2.2 Hz, *C*$_{ipso}$-*arom*, L^1), 150.5 (d, J_{CP} = 8.4 Hz, *C*$_{ipso}$,*C*OP- L^1), 152.4 (d, J_{CP} = 13.5 Hz, *C*$_{ipso}$,*C*OP-L^1), 177.5 [d, J_{CP} = 5.3 Hz, CH(*C*O$_2$CH$_3$)$_2$], 179.2 [d, J_{CP} = 2.0 Hz, CH(*C*O$_2$CH$_3$)$_2$]. ^{31}P{^{1}H} NMR (121.48 MHz, C$_6$D$_6$, 298 K): δ 102.5. IR (KBr, cm^{-1}): 1718, 1619 [ν_{CO}]. Anal. Calcd for $C_{29}H_{35}ClNO_6OsP$: C, 46.43; H, 4.70; N, 1.87. Found: C, 46.64; H, 4.91; N, 1.93.

Reaction of OsCl$_2$(η^6-*p*-cymene)L^2 with Na[CH(CO$_2$Me)$_2$]: Formation of Os{κ^1-*C*^{3}-[CH(CO$_2$Me)$_2$]}Cl(η^6-*p*-cymene)L^2 (13). Freshly prepared sodium dimethylmalonate (1.69 mmol, 3 mL, 0.56 M in THF) was added to a stirred suspension of OsCl$_2$(η^6-*p*-cymene)L^2 (**3**; 320 mg, 0.42 mmol) in THF (5 mL) and the mixture stirred at rt for 3 h. The complex was purified as described for complex **12** and isolated as a dark yellow solid (7:3 mixture of two diastereomers; 226 mg, 0.26 mmol, 63% yield). *Major isomer*: ^{1}H NMR (400 MHz, C$_6$D$_6$, 298 K) δ 0.71 [d, J_{HH} = 6.8 Hz, 3 H, (C*H*$_3$)$_2$CH, *p*-cymene], 0.97 [d, J_{HH} = 6.8 Hz, 3 H, (C*H*$_3$)$_2$CH, *p*-cymene], 2.05 (d, J_{HH} = 1.2 Hz, 3 H, C*H*$_3$, *p*-cymene), 2.38 [sept, J_{HH} = 6.8 Hz, 1 H, (CH$_3$)$_2$C*H*, *p*-cymene], 2.89 [d, J_{HP} = 8.4 Hz, 6 H, N(C*H*$_3$)$_2$], 3.47, 3.64 [both s, 3 H, CH(CO$_2$C*H*$_3$)$_2$], 4.26 (d, J_{HH} = 5.4 Hz, 1 H, C*H*-*arom*, *p*-cymene), 4.83 (d, J_{HH} = 5.6 Hz, 1 H, C*H*-*arom*, *p*-cymene), 4.94 [d, J_{HP} = 7.6 Hz, 1 H, C*H*(CO$_2$CH$_3$)$_2$], 5.00 (d, J_{HH} = 5.6 Hz, 1 H, C*H*-*arom*, *p*-cymene), 5.81 (d, J_{HH} = 5.4 Hz, 1 H, C*H*-*arom*, *p*-cymene), 5.85−7.63 (11 H, C*H*-*arom*, L^2), 8.12 (d, J_{HH} = 8.8 Hz, 1 H, C*H*-*arom*, L^2).

Table 2. Crystal Data and Data Collection and Refinement Parameters for 3, 9, 11, and 12

	3	9	11	12
		Crystal Data		
formula	$C_{32}H_{32}Cl_2NO_2OsP$ 2xCH_2Cl_2	$C_{22}H_{34}Cl_2O_2Os_2$	$C_{20}H_{28}O_8Os$	$C_{29}H_{35}ClNO_6OsP$
molecular wt	928.54	781.79	586.62	750.20
color and habit	orange, block,	yellow, block	yellow, block	yellow, prism
symmetry, space group	triclinic, *P*1	monoclinic, $P2_1/c$	monoclinic, $P2_1/c$	orthorhombic, *Pbca*
a, Å	11.3914(17)	9.0720(15)	12.114(2)	17.820(3)
b, Å	12.7982(19)	16.049(3)	12.583(2)	16.545(2)
c, Å	13.0920(19)	8.2477(14)	14.151(3)	19.229(3)
α, deg	90.109(3)			
β, deg	107.610(2)	102.549(3)	100.732(3)	
γ, deg	103.228(3)			
V, Å^3	1765.7(5)	1172.1(3)	2119.3(6)	5669.5(14)
Z	2	2	4	8
D_{calc}, g cm^{-3}	1.746	2.215	1.839	1.758
		Data Collection and Refinement		
diffractometer *λ*(Mo Kα), Å	Bruker Smart APEX 0.71073			
monochromator	graphite oriented			
scan type	*ω* scans			
μ, mm^{-1}	4.143	11.073	6.060	4.693
2*θ*, range deg	3, 57	3, 57	3, 57	3, 57
temp, K	100	100	105	100
no. of data collect	15 938	14 482	25 845	67 418
no. of unique data	14 312 (R_{int} = 0.027)	2904 (R_{int} = 0.047)	5228 (R_{int} = 0.046)	7148 (R_{int} = 0.085)
no. of params/restrains	775/18	131/0	272/0	361/2
R_1[a] [$F^2 > 2\sigma(F^2)$]	0.0459	0.0302	0.0316	0.0526
wR_2[b] [all data]	0.1131	0.0630	0.0716	0.1039
S[c][all data]	1.028	0.951	1.097	1.195

[a] $R_1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2(F^2) = \{\sum[w(\sum F_o^2 - F_c^2)^2]/\sum w(F_o^2\}\}^{1/2}$. [c] Goof = $S = \{\sum[F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where *n* is the number of reflections and *p* is the number of refined parameters.

$^{13}C\{^1H\}$ NMR (100.56 MHz, C_6D_6, 298 K): *δ* 17.2 (s, *C*H_3, *p*-cymene), 17.4 [d, J_{CP} = 20.1 Hz, *C*H$(CO_2CH_3)_2$], 21.2, 23.6 [both s, $(CH_3)_2$CH, *p*-cymene], 30.6 [s, $(CH_3)_2$*C*H, *p*-cymene], 38.6 [d, J_{CP} = 0.7 Hz, N$(CH_3)_2$], 50.0, 50.2 [both s, CH$(CO_2CH_3)_2$], 75.8 (s, *C*H-*arom*, *p*-cymene), 80.0 (d, J_{CP} = 5.1 Hz, *C*H-*arom*, *p*-cymene), 83.3 (s, *C*H-*arom*, *p*-cymene), 88.6 (d, J_{CP} = 8.6 Hz, *C*H-*arom*, *p*-cymene), 96.5 (s, CH_3C_{ipso}, *p*-cymene), 106.2 [s, $(CH_3)_2CHC_{ipso}$, *p*-cymene], 121.4 (d, J_{CP} = 1.5 Hz, *C*H-*arom*, L^2), 123.2 (d, J_{CP} = 2.3 Hz, C_{ipso}, L^2), 123.9 (d, J_{CP} = 3.1 Hz, C_{ipso}, L^2), 124.9 (d, J_{CP} = 2.8 Hz, *C*H-*arom*, L^2), 125.5, 126.6, 126.8, 127.0, 127.5 (s, *C*H-*arom*, L^2) 127.9, 128.2 (both s, C_{ipso}, L^2), 128.3, 128.5, 128.7, 130.0, 130.5, (all s, *C*H-*arom*, L^2), 131.6, 133.3 (both s, C_{ipso}, L^2), 150.8, 151.0 (both s, C_{ipso}, *C*OP-L^2), 177.0 [d, J_{CP} = 4.9 Hz, CH(*C*$O_2CH_3)_2$], 179.8 [s, CH(*C*$O_2CH_3)_2$]. $^{31}P\{^1H\}$ NMR (161.99 MHz, C_6D_6, 298 K): *δ* 106.3. *Minor isomer*: ^{1}H NMR (400 MHz, C_6D_6, 298 K) *δ* 1.06 [d, J_{HH} = 6.8 Hz, 3 H, $(CH_3)_2$CH, *p*-cymene], 1.12 [d, J_{HH} = 7.2 Hz, 3 H, $(CH_3)_2$CH, *p*-cymene], 1.93 (s, 3 H, C*H*$_3$, *p*-cymene), 2.29 [d, J_{HP} = 10 Hz, 6 H, N$(CH_3)_2$], 2.75 [sept, J_{HH} = 6.8 Hz, 1 H, $(CH_3)_2$C*H*, *p*-cymene], 2.86, 3.55 [both s, 3 H, CH$(CO_2CH_3)_2$], 5.09 (d, J_{HH} = 5.4 Hz, 1 H, C*H*-*arom*, *p*-cymene), 5.37 (d, J_{HH} = 5.4 Hz, 1 H, C*H*-*arom*, *p*-cymene), 5.43 [d, J_{HP} = 6.4 Hz, 1 H, C*H*$(CO_2CH_3)_2$], 5.60 (d, J_{HH} = 6.0 Hz, 1 H, C*H*-*arom*, *p*-cymene), 5.98 (d, J_{HH} = 6.0 Hz, 1 H, C*H*-*arom*, *p*-cymene), 6.83−7.66 (11 H, C*H*-*arom*, L^2), 7.87 (d, J_{HH} = 8.8 Hz, 1 H, C*H*-*arom*, L^2). $^{13}C\{^1H\}$ NMR (100.56 MHz, C_6D_6, 298 K): *δ* 16.9 (s, *C*H_3, *p*-cymene), 19.5 [d, J_{CP} = 23.1 Hz, *C*H$(CO_2CH_3)_2$], 22.0, 22.6 [both s, $(CH_3)_2$CH, *p*-cymene], 30.4 [s, $(CH_3)_2$*C*H, *p*-cymene], 38.7 [d, J_{CP} = 5.8 Hz, N$(CH_3)_2$], 49.7, 50.3 [both s, CH$(CO_2CH_3)_2$], 76.1 (s, *C*H-*arom*, *p*-cymene), 81.4 (d, J_{CP} = 2.4 Hz, *C*H-*arom*, *p*-cymene), 81.9 (d, J_{CP} = 12.5 Hz, *C*H-*arom*, *p*-cymene), 89.6 (d, J_{CP} = 4.8 Hz, *C*H-*arom*, *p*-cymene), 92.0 (s, $CH_3C_{ipso,}$ *p*-cymene), 96.0 [s, $(CH_3)_2CHC_{ipso}$, *p*-cymene], 121.7 (d, J_{CP} = 2.2 Hz, *C*H-*arom*, L^2), 123.5, 123.6 (both s, C_{ipso}, L^2), 124.2 (d, J_{CP} = 4.1 Hz, *C*H-*arom*, L^2), 124.9, 125.5, 126.2, 126.8, 127.4, 127.6, (all s, *C*H-*arom*, L^2) 128.4 (s, C_{ipso}, L^2), 128.5 (s, *C*H-*arom*, L^2), 128.6, 130.1, 130.5 (all s, *C*H-*arom*, L^2), 133.5 (d, J_{CP} = 1.2 Hz, C_{ipso}, L^2), 133.9 (d, J_{CP} = 1.6 Hz, C_{ipso}, L^2), 149.0, 149.1 (both s, C_{ipso}, *C*OP-L^2), 177.4, 179.0 [both s, CH(*C*$O_2CH_3)_2$]. $^{31}P\{^1H\}$ NMR (161.99 MHz, C_6D_6, 298 K): *δ* 106.1. IR (KBr, cm^{-1}): 1732, 1619 [ν_{CO}]. Anal. Calcd for $C_{37}H_{39}ClNO_6OsP$: C, 52.01; H, 5.07; N, 1.64. Found: C, 52.06; H, 4.92; N, 1.62.

Reaction of Os{κ^1-*C*^{3}-[CH$(CO_2Me)_2$]}Cl(η^6-*p*-cymene)L^2 with Na[CH$(CO_2Me)_2$]. Formation of Os{κ^1-*C*^{3}-[CH$(CO_2Me)_2$]}{κ^2-*O,O*-[CH$(CO_2Me)_2$]}(η^6-*p*-cymene) (11). A solution of **12** (50 mg, 0.07 mmol) in THF (3 mL) was treated with a freshly prepared solution of sodium dimethylmalonate (0.53 mmol, 3 mL, 0.18 M in THF) and refluxed for 24 h. After this time, the ^{1}H NMR spectrum of the reaction mixture showed the presence of complex **11**.

General Procedure for the Os-Catalyzed Allylic Alkylation. A solution of the catalyst (0.01 mmol, 4 mol % in Os) in THF (1 mL) was treated with a second solution of the substrate (0.26 mmol) in THF (1 mL). The resulting mixture was stirred for 5 min. Then a freshly prepared solution of sodium dimethylmalonate (0.52 mmol, 2 mL, 0.26 M in THF), obtained as described above, was added and the resulting mixture stirred at 60 °C. See Table 1 for reaction times, yields, and molar ratio of products, determined on the basis of ^{1}H NMR experiments.

Conditions for the Catalysis Performed in an NMR Tube. A solution of the catalyst (2.6×10^{-3} mmol, 4 mol % in Os) and the substrate (**5a**; 12.5 mg, 6.5×10^{-2} mmol) in THF-d_8 (0.5 mL) was treated with a freshly prepared solution of sodium dimethylmalonate (0.13 mmol, 0.5 mL, 0.26 M in THF-d_8). The resulting mixture was heated at 60 °C and monitored by ^{1}H NMR.

Structural Analysis of Complexes 3, 9, 11, and 12. X-ray data were collected for all complexes on a Bruker Smart APEX CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube source (Mo radiation, λ = 0.71073 Å) operating at 50 kV and 30 mA or 40 (**9**) mA. Data were collected over the complete sphere by a combination of four sets. Each frame exposure time was 10 s covering 0.3° in *ω*. Data were corrected for absorption by using a multiscan method applied with the SADABS program.[39] The structures of all compounds were solved by the Patterson method. Refinement, by full-matrix least-squares on F^2 with SHELXL97,[40] was similar for all complexes, including isotropic and subsequently anisotropic displacement parameters.

The hydrogen atoms were observed or calculated and refined freely or using a restricted riding model. All the highest electronic residuals were observed in close proximity of the Os centers and make no chemical sense. For **3**, disordered dichloromethane was observed in the asymmetric unit as crystallization solvents. Selected crystal data and data collection and refinement parameters for **3**, **9**, **11**, and **12** are given in Table 2.

Acknowledgment. Financial support from the MEC of Spain (Proyect CTQ2005-00656) and Consolider Ingenio 2010 (CSD2007-00006) is acknowledged. We thank Antonio Pizzano and Andrés Suárez (Instituto de Investigaciones Químicas, Sevilla) for HPLC measurements. C.G.-Y. thanks the Spanish MEC and the University of Zaragoza for funding through the "Ramón y Cajal" program.

Supporting Information Available: CIF file giving crystal data for compounds **3**, **9**, **11**, and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM800460H

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