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## Synthesis of Ruthenium(II) 1,2,3-Trimethylindenyl Complexes: X-ray Crystal Structure of $[Ru(=C=C=CPh_2)(\eta^5\text{-}1,2,3\text{-}Me_3C_9H_4)(CO)(PPh_3)][BF_4]$

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*Summary: The first ruthenium(II) 1,2,3-trimethylindenyl complexes have been prepared, including allenylidene, alkynyl, and alkenylcarbene derivatives. The X-ray crystal structure of* $[Ru(=C=C=CPh_2)(\eta^5\text{-}1,2,3\text{-}Me_3C_9H_4)(CO)(PPh_3)][BF_4]$ *is described.*

The chemistry of half-sandwich methyl-substituted indenyl complexes of the late transition metals has been scarcely studied compared to that of the analogous $C_5Me_5$ derivatives.[1] In particular, as far as we are aware, no methylindenyl ruthenium complexes have yet been described, in spite of the potential interest of indenyl complexes based on the enhanced reactivity (generally associated with the *indenyl effect*) with respect to the analogous cyclopentadienyl derivatives. During the last few years, we have described[2−4] the synthesis of novel ruthenium(II) $\eta^5$-indenyl complexes and have investigated the influence of the indenyl ring in the chemical behavior of unsaturated carbene derivatives. Herein, we report the first ruthenium(II) 1,2,3-trimethylindenyl complexes including alkynyl, alkenyl−carbene, and allenylidene derivatives containing the fragments $[Ru(\eta^5\text{-}1,2,3\text{-}Me_3C_9H_4)LL']$ (L = CO, L′ = $PR_3$; L-L′ = bis(diphenylphosphino)methane (dppm)).

As expected, the half-sandwich moiety $[Ru(\eta^5\text{-}1,2,3\text{-}Me_3C_9H_4)LL']^+$, containing a mixed CO−$PR_3$ system or the electron-releasing chelating ligand bis(diphenylphosphino)methane (dppm) as the ancillary ligands, is able to stabilize carbene and allenylidene moieties. A mixture of $[Ru(\eta^5\text{-}1,2,3\text{-}Me_3C_9H_4)BrLL']$[5] (L = CO, L′ = $PPh_3$, $P^iPr_3$; L-L′ = dppm) and $AgBF_4$ in $CH_2Cl_2$ at room temperature reacts with 1,1-diphenyl-2-propyn-1-ol to give, after filtration of AgBr, the violet allenylidene complexes $[Ru(=C=C=CPh_2)(\eta^5\text{-}1,2,3\text{-}Me_3C_9H_4)(CO)L][BF_4]$ (**1**, **2**; L = $PPh_3$, $P^iPr_3$) and $[Ru(=C=C=CPh_2)(\eta^5\text{-}1,2,3\text{-}Me_3C_9H_4)(dppm)][BF_4]$ (**3**) (65−85% yield) (Scheme 1). The spectroscopic properties of **1**−**3** are consistent[6a] with the presence of the allenylidene moiety,[2c] in particular, the $\nu$(C=C=C) IR absorption (1924−1993

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(2) (a) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Lastra, E.; Borge, J.; García-Granda, S. *Organometallics* **1994**, *13*, 745. (b) Gamasa, M. P.; Gimeno, J; Martín-Vaca, B. M.; Borge, J.; García-Granda, S.; Pérez-Carreño, E. *Organometallics* **1994**, *13*, 4045. (c) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; González-Cueva, M.; Lastra, E.; Borge, J.; García-Granda, S.; Pérez-Carreño, E. *Organometallics* **1996**, *15*, 2137.

(3) Gamasa, M. P.; Gimeno, J.; González-Bernardo, C.; Martín-Vaca, B. M.; Monti, D.; Bassetti, M. *Organometallics* **1996**, *15*, 302.

(4) (a) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Lastra, E. *J. Organomet. Chem.* **1994**, *474*, C27. (b) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Borge, J.; García-Granda, S. *J. Chem. Soc., Chem. Commun.* **1994**, 2495.

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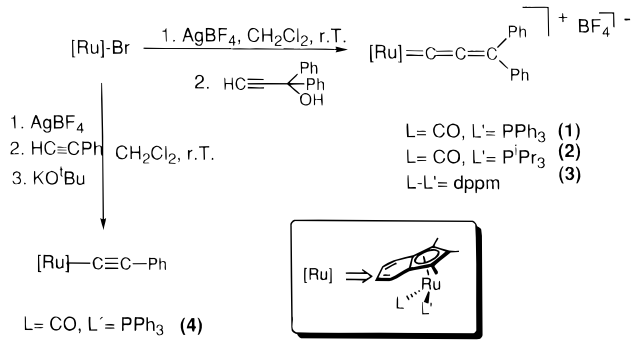
**Scheme 1. Synthesis of Allenylidene and Alkynyl Complexes**




cm$^{-1}$) and the typical chemical shift, $\delta$, in the $^{13}$C NMR spectrum of the Ru=C carbon nucleus at 287.33−289.79 ppm ($^2J_{CP}$ = 15.3−16.4 Hz).[2a,2c]

Under similar reaction conditions, [Ru($\eta^5$-1,2,3-$Me_3C_9H_4$)Br(CO)($PPh_3$)] also reacts with phenylacetylene but a mixture containing the corresponding vinylidene and the $\pi$-bonded alkyne complexes is obtained. $^{31}$P{$^1$H} NMR spectrum of the mixture confirms the presence of both species. All attempts to isolate the vinylidene species have failed.[7] The formation of the transient vinylidene complex is assessed by the addition of potassium *tert*-butoxide to this mixture, which leads, after deprotonation, to the alkynyl complex [Ru(-C≡C-CPh)($\eta^5$-1,2,3-$Me_3C_9H_4$)(CO)($PPh_3$)] (**4**) (75% yield).[6]

It is well-known that the electrophilicity of the $C_\alpha$ and $C_\gamma$ atoms of the allenylidene group depends on the electronic nature of the metal fragment.[8] We have shown[2c] that the indenyl group in the complex [Ru{=C=C=$CPh_2$}($\eta^5$-$C_9H_7$)($PPh_3$)$_2$]$^+$ exhibits a steric influence on the $C_\alpha$ atom. As a consequence of the preferred *cis* conformation of the indenyl ring with respect to the unsaturated carbene chain, the benzo ring of the indenyl group is over the $C_\alpha$ atom.[9] In order to get information on the preferred conformation of the analogous 1,2,3-$Me_3C_9H_4$ group and on the overall protection of the $C_\alpha$ atom, a single-crystal X-ray structural determination of complex **1** was carried out.[10]

The structure shows (Figure 1) the typical pseudo-octahedral three-legged piano-stool geometry, with a nearly linear allenylidene group coordinated to the ruthenium atom. Bond distances in the allenylidene

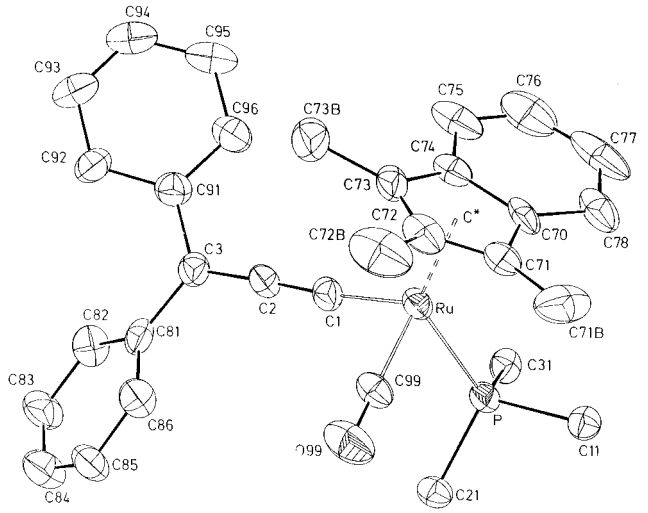



**Figure 1.** ORTEP drawing of **1**. Selected bond distances (Å) and angles (deg): Ru−C1, 1.92(1); Ru−C99, 1.83(1); Ru−P, 2.349(3); Ru−C*, 1.93(1); C99−O99, 1.15(1); C1−C2, 1.26(1); C2−C3, 1.35(2); C3−C81, 1.47(2); C3−C91, 1.48(2); C99−Ru−C1, 92.1(5); C99−Ru−P, 86.8(4); C1−Ru−P, 92.5(3); O99−C99−Ru, 176.(1); C2−C1−Ru, 172.-(1); C1−C2−C3, 176.(1); C2−C3−C81, 120.(1); C2−C3−C91, 120.(1). C* = centroid of the indenyl ring.

(5) The halide complexes [Ru($\eta^5$-1,2,3-$Me_3C_9H_4$)BrLL′] (L = CO, L′ = $PPh_3$, $P^iPr_3$; L-L′ = bis(diphenylphosphino)methane (dppm)) are easily prepared in high yields from [Ru($\eta^5$-1,2,3-$Me_3C_9H_4$)X(CO)$_2$] by substitution of one or two carbonyl groups with the appropriate phosphine. Gamasa, M. P.; Gimeno, J.; González-Bernardo, C. Unpublished results.

(6) (a) Synthesis of allenylidene complexes **1**−**3**. General procedure: A mixture of [Ru($\eta^5$-1,2,3-$Me_3C_9H_4$)BrLL′] (0.80 mmol) and $AgBF_4$ (0.88 mmol) in $CH_2Cl_2$ (70 mL) was stirred under nitrogen for 15 min at room temperature in the absence of light. After the AgBr formed was filtered, HC≡CC(OH)$Ph_2$ (2.4 mmol) was added to the solution, whose color changed immediately from yellow to violet. The mixture was stirred for 15 min, the solvent evaporated, and the solid residue washed several times with diethyl ether. A violet solid was obtained (yield: 65−85%). Spectroscopic data for complex **1**. $^{31}$P{$^1$H} NMR ($\delta$, ppm): 48.20 (s). $^1$H NMR ($\delta$, ppm): 1.85 (s, 3H, Me), 2.04 (s, 3H, Me), 2.21 (d, 3H, $^4J_{HP}$ = 1.0 Hz, Me), 6.78−7.84 (m, 29H, H-4−7, $PPh_3$, Ph). $^{13}$C{$^1$H} NMR ($\delta$, ppm): 9.42 (Me), 10.47 (Me), 11.05 (Me), 92.74 (d, $^2J_{CP}$ = 4.3 Hz), 94.37 (C-1 and C-3), 108.47, 112.97, 115.74 (C-2, C-3a, and C-7a), 121.02, 123.45 (C-4,7 or C-5,6), 129.08−142.2 (m, $PPh_3$, Ph, C-4,7 or C-5,6), 166.94 ($C_\gamma$), 183.62 (d, $^3J_{CP}$ = 1.8 Hz, $C_\beta$), 201.09 (d, $^2J_{CP}$ = 17.0 Hz, CO), 289.29 (d, $^2J_{CP}$ = 15.9 Hz, $C_\alpha$). (b) Spectroscopic data of complexes **4** and **5**. **4**: $^{31}$P{$^1$H} NMR ($\delta$, ppm) 54.77 (s). $^1$H NMR ($\delta$, ppm): 1.53 (s, 3H, Me), 1.94 (d, 3H, $^4J_{HP}$ = 1.7 Hz, Me), 2.04 (s, 3H, Me), 6.63 (m, 1H), 6.71 (m, 1H), 6.82 (m, 1H), 6.96−7.40 (m, 21H, H-4−7, $PPh_3$, Ph). $^{13}$C{$^1$H} NMR ($\delta$, ppm): 8.59 (Me), 9.95 (Me), 11.16 (Me), 85.56, 86.23 (d, $^2J_{CP}$ = 5.0 Hz, C-1 and C-3), 105.24, 109.01, 110.50 (d, $^2J_{CP}$ = 8.1 Hz, C-2, C-3a, and C-7a), 109.87 (d, $^2J_{CP}$ = 25.0 Hz, $C_\alpha$), 121.78−134.82 (m, C-4−7, $C_\beta$, $PPh_3$, Ph), 207.25 (d, $^2J_{CP}$ = 18.6 Hz, CO). **5**: $^{31}$P{$^1$H} NMR ($\delta$, ppm) 44.76 (bs). $^1$H NMR ($\delta$, ppm): 1.46 (s, 3H, Me), 1.76 (s, 3H, Me), 1.85 (s, 3H, Me), 4.00 (m, 3H, OMe), 5.09 (s, 1H, −CH=), 6.56−7.70 (m, 29H, H-4−7, $PPh_3$, Ph). $^{13}$C{$^1$H} NMR ($\delta$, ppm): 8.95 (Me), 10.19 (Me), 10.53 (Me), 67.63 (OMe), 88.30 (C-1 and C-3), 106.03, 116.99 (C-2, C-3a, and C-7a), 119.10 (Ind), 124.25 (Ind), 127.89 (Ind), 125.62−139.77 (m, Ind, −CH=, $PPh_3$, Ph), 145.48 (=$CPh_2$), 204.15 (d, $^2J_{CP}$ = 15.3 Hz, CO), 298.58 (m, $C_\alpha$). Ind = C-4,5,6, or 7.

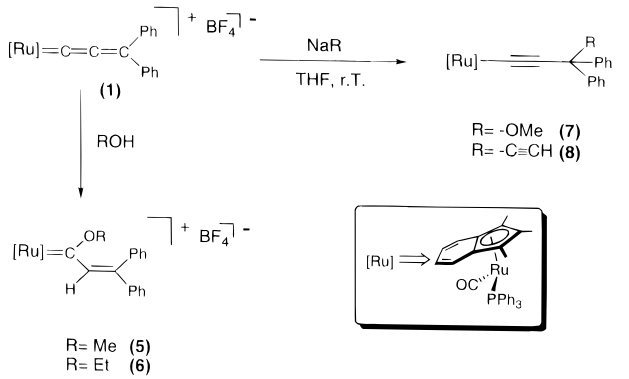
(7) (a) A similar equilibrium has also been observed at room temperature for the analogous ruthenium fragment [Ru($\eta^5$-$C_5H_5$)(CO)($PPh_3$)]$^+$: Nombel, P.; Lugan, N.; Mathieu, R. *J. Organomet. Chem.* **1995**, *503*, C22. (b) $\eta^2$-Alkyne complexes have been isolated: Lomprey, J. R.; Selegue, J. P. *J. Am. Chem. Soc.* **1992**, *114*, 5518. (c) Studies on the ready isomerization of [Fe($\eta^5$-$C_5H_5$)(CO)$_2$(=C=CRR′)]$^+$ in the corresponding $\eta^2$-alkyne [Fe($\eta^5$-$C_5H_5$)(CO)$_2$($\eta^2$-RC≡CR′)]$^+$ have been reported: Bly, R. S.; Zhong, Z.; Kane, C.; Bly, R. K. *Organometallics* **1994**, *13*, 899.

(8) (a) The following allenylidene complexes add alcohols at $C_\alpha$. (i) [Ru(=C=C=$CR_2$)($\eta^6$-arene)Cl($PR'_3$)]$^+$: Pilette, D.; Ouzzine, K.; Le Bozec, H.; Dixneuf, P. H.; Rickard, C. E. F.; Roper, W. R. *Organometallics* **1992**, *11*, 809. (ii) [Ru(=C=C=$CPh_2$)($\eta^5$-$C_5H_5$)(CO)($P^iPr_3$)]$^+$: Esteruelas, M. A.; Gómez, A. V.; Lahoz, F. J.; López, A. M.; Oñate, E.; Oro, L. A. *Organometallics* **1996**, *15*, 3423. (b) The allenylidene group is stable toward methanol or ethanol in the following complexes. (i) [Ru(=C=C=$CPh_2$)($\eta^5$-$C_5H_5$)($PMe_3$)$_2$]$^+$: Selegue, J. P. *Organometallics* **1982**, *1*, 217. (ii) [Ru(=C=C=$CR_2$)($\eta^5$-$C_9H_7$)($PPh_3$)$_2$]$^+$ (R = Ph, $R_2$ = $C_{12}H_8$; $C_{12}H_8$ = 2,2′-biphenyldiyl): ref 2c. (iii) [Ru(=C=C=$CPh_2$)Cl($NP_3$)]$^+$ ($NP_3$ = $N(CH_2CH_2PPh_2)_3$): Wolinska, A.; Touchard, P. H.; Dixneuf, P. H.; Romero, A. *J. Organomet. Chem.* **1991**, *420*, 217. (iv) [Ru(=C=C=CRR′) Cl(dppm)$_2$]$^+$ (R = R′ = Ph; R = H, R′ = Ph, *p*-PhCl, *p*-PhOMe): Pirio, N.; Touchard, D.; Toupet, L.; Dixneuf, P. H. *Organometallics* **1995**, *14*, 4920. (v) [Ru(=C=C=CRR′)$Cl_2$\{$\kappa P$-$^i$Pr$_2$$PCH_2CO_2$-Me\}\{$\kappa^2P,O$-$^i$Pr$_2$$PCH_2CO_2$Me\}] (R = Ph, R′ = Ph, *o*-Tol): Werner, H.; Stark, A.; Steinert, P.; Grünwald, C.; Wolf, J. *Chem. Ber.* **1995**, *128*, 49.

(9) EHMO calculations are in accordance with these preferred conformations in the solid state. Reference 2c.

(10) Crystal data: [$C_{46}H_{38}OPRu$][$BF_4$]; $M_r$ = 825.61; monoclinic; space group $P2_1/n$; $a$ = 14.834(6) Å, $b$ = 17.893(5) Å, $c$ = 14.93(1) Å; $\beta$ = 95.89(7)°; $V$ = 3941(4) Å$^3$; $Z$ = 4; $\rho_{calcd}$ = 1.391 g cm$^{-3}$; $F$(000) = 1688; $\mu$ = 0.49 mm$^{-1}$; violet crystal (0.13 × 0.36 × 0.23 mm); 7466 reflections measured, 6917 used in refinement; full-matrix least-squares refinement on $F^2$; the $BF_4^-$ anion exhibited severe structural disorder; final R1 = 0.062 and wR2 = 0.154 (both for $I > 2\sigma(I)$); the function minimized was $[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.1015*P)^2 + (6.92*P)]$ where $P = (\mathrm{Max}(F_o^2,0) + 2*F_c^2)/3$ with $\sigma^2$ ($F_o^2$) from counting statistics; number of parameters refined 470; residual electronic density less than 0.91 e Å$^{-3}$; maximum parameter shift to esd ratio 0.051; $T$ = 293 K; Enraf-Nonius CAD4 diffractometer; $\lambda$ (Mo K$\alpha$) = 0.710 73 Å, $\omega-2\theta$ scan technique (2° < $\theta$ < 25°).

**Scheme 2. Reactivity of Complex 1**




chain (Ru−$C_\alpha$ 1.92(1) Å, $C_\alpha$−$C_\beta$ 1.26(1) Å, $C_\beta$−$C_\gamma$ 1.35(1) Å) show the usual contribution of the resonant form [Ru]−C≡$CC^+R_2$. The most interesting feature is the conformation of the indenyl ligand, which shows an orientation between the formally *cis* and *trans* orientation with respect to the allenylidene group,[11] in contrast to the *cis* orientation shown by the indenyl ligand in [Ru{=C=C=$CPh_2$}($\eta^5$-$C_9H_7$)($PPh_3$)$_2$]$^+$.[2c] Assuming that no rotation of the indenyl ring around the ruthenium atom takes place,[12] this orientation should facilitate the approach of the nucleophiles to the electrophilic sites of the allenylidene chain. On the basis of these expectations, we have examined the influence of the ancillary ligands of the metal fragment [Ru($\eta^5$-1,2,3-$Me_3C_9H_4$)LL′] on the reactivity of the allenylidene chain.

In accordance with the inertness of the related complex [Ru(=C=C=$CPh_2$)($\eta^5$-$C_9H_7$)($PPh_3$)$_2$][$PF_6$] toward alcohols, complex **3** is also unreactive toward refluxing methanol and other alcohols. In contrast, complex **1** reacts with methanol and ethanol to give the α,β-unsaturated-alkoxycarbene complexes **5** and **6** (Scheme 2). Analytical and spectroscopic data are consistent with this formulation.[6b,13] The regioselective nucleophilic addition to the $C_\alpha$ atom of the allenylidene chain in complex **1** to give the carbene species is probably promoted by the presence of the carbonyl group, which is less sterically demanding and more π-accepting than triphenylphosphine.

However, complex **1** reacts with anionic nucleophiles in a different way, since only the addition to the $C_\gamma$ atom of the allenylidene chain takes place. Thus, the treatment of **1** with NaOMe and NaC≡CH leads to the alkynyl complexes **7** and **8** (Scheme 2). IR and NMR ($^1$H, $^{31}$P, $^{13}$C) data support the proposed formulations. This behavior is in agreement with that of the related complex [Ru(=C=C=$CPh_2$)($\eta^5$-$C_9H_7$)($PPh_3$)$_2$][$PF_6$], which also undergoes nucleophilic additions to give analogous alkynyl complexes [Ru($\eta^5$-$C_9H_7$){C≡C−C(Nu)$Ph_2$}($PPh_3$)$_2$] (Nu = OMe, C≡CPh).[4a]

In summary, it is shown that nucleophilic additions to the allenylidene chain in half-sandwich ruthenium(II) indenyl complexes depend on the steric and electronic properties of the ancillary ligands. It is also apparent that the CO/$PPh_3$ combination not only determines the greater electrophilicity of the allenylidene chain but also favors a less sterically demanding orientation of the indenyl ring over the $C_\alpha$ atom of the allenylidene chain (Figure 1). Finally, it is worth noting the different outcome of the nucleophilic additions shown by complex **1** depending on the nature of the incoming nucleophile. This raises the question of the factors which are controlling the regioselectivity. Further studies on the reactivity of trimethylindenyl ruthenium(II) allenylidene complexes and on the scope of the nucleophilic additions along with theoretical calculations on the distribution of LUMO and HOMO on the allenylidene chain are in progress.

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**Supporting Information Available:** Text giving synthetic details and characterization data for **1**−**8** and text and tables giving details of the X-ray diffraction study of **1** (22 pages). Ordering information is given on any current masthead page.

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(11) The orientation may be established by the conformational angle (CA), defined as the dihedral angle between the planes C** (centroid of the benzo ring of the indenyl ligand), C*, and Ru and C*, Ru, and C(1) of 79.6(5)° (0° and 180° for the *cis* and *trans* orientation, respectively).

(12) A space-filling representation of complex **1** indicates that the potential rotation of the indenyl ring around the ruthenium atom is hindered by the phenyl rings of the triphenylphosphine and the allenylidene chain: Borge, J.; García-Granda, S. Unpublished results.

(13) The structure of **6** has been confirmed by an X-ray diffraction study (Borge, J.; García-Granda, S. Personal communication).