

Preparation and Characterization of an Isometallabenzene with the Structure of a 1,2,4-Cyclohexatriene

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Benzene is an archetypal aromatic compound and one of the best known molecules of this type. Metallabenzenes are a class of benzene analogues on which a CH group has been formally replaced by a transition metal and its associated ligands (Chart 1).¹ The L_nM fragment of the six-membered metallacycle mainly includes Os² and Ir.³ Recently, Pt metallabenzene has been also reported.⁴

1,2,4-Cyclohexatriene (**IIa** in Chart 2) is a short-lived strained allene isomer of benzene.⁵ The cyclic **IIa** structure has been proposed as the key intermediate in Diels–Alder reactions of enynes with alkynes, and in several rearrangements.⁶ Conclusive evidence for **IIa** was obtained by the isolation of trapping products, after **IIa** had been generated in the presence of activated olefins.⁷ In contrast to benzene and its derivatives, analogue metalla-**IIa** structures in which the 3-CH group is formally replaced by a L_nM transition metal fragment (**IIb** in Chart 2) are unknown.

We wish to report the preparation and characterization of the first isometallabenzene with the structure of a 1,2,4-cyclohexatriene. This novel compound, **3** in Scheme 1, has been obtained by a two-step procedure, starting from the elongated dihydrogen complex **1**.⁸

Treatment at $-50\text{ }^\circ\text{C}$ of dichloromethane solutions of **1** with 2.0 equiv of $\text{HBF}_4\cdot\text{OEt}_2$ and 4.5 equiv of phenylacetylene affords the $16e^-$ -alkenyl-alkynyl-carbyne intermediate **2**, which was isolated as a green solid in 78% yield.⁹ Figure 1 shows a view of the structure of the cation of this species, which is notable not only for the unsaturated character of the osmium atom¹⁰ but also because it contains three different metal–carbon bonds: two osmium–carbon single bonds, Os–C(sp²) (Os–C(1) = 2.036(9) Å) and Os–C(sp) (Os–C(9) = 2.029(8) Å), and a triple Os–C(sp) bond (Os–C(17) = 1.699(7) Å). The geometry around the osmium atom can be described as a distorted trigonal bipyramid with apical phosphines (P(1)–Os–P(2) = 166.71(7)°) and inequivalent angles within the Y-shaped equatorial plane (C(17)–Os–C(9) = 114.8(3)°, C(17)–Os–C(1) = 101.1(4)°, and C(9)–Os–C(1) = 144.1(3)°). The ³¹P{¹H} NMR spectrum is consistent with this geometry, and in dichloromethane-*d*₂ at $-50\text{ }^\circ\text{C}$, it contains a singlet at 46.5 ppm. In agreement with the presence of the carbyne, alkenyl, and alkynyl ligands, the ¹³C{¹H} NMR spectrum shows resonances at 275.1 (C(17)), 155.7 (C(1)), and 140.8 (C(9)) ppm, respectively.

In dichloromethane at temperatures higher than $-30\text{ }^\circ\text{C}$, complex **2** is unstable and evolves into a complex mixture of unidentified products. However, in the presence of an excess of NaCl, the evolution takes place in a controlled way, and the cyclic-allene derivative **3** is formed.¹¹

The structure of **3** has two chemically equivalent but crystallographically independent molecules of complex in the asymmetric unit (enantiomers). A drawing of the *R*-enantiomer is shown in Figure 2. The bond lengths in the sequence C(17)–C(24)–Os(1)–C(1)–C(9)–C(10)–C(17) (C(59)–C(66)–Os(2)–C(43)–C(51)–C(52)–C(59) in *S*) are 1.331(6), 1.806(4), 2.043(4), 1.335(6), 1.513(6), and 1.542(6) Å (1.330(6), 1.798(5), 2.057(5), 1.328(7),

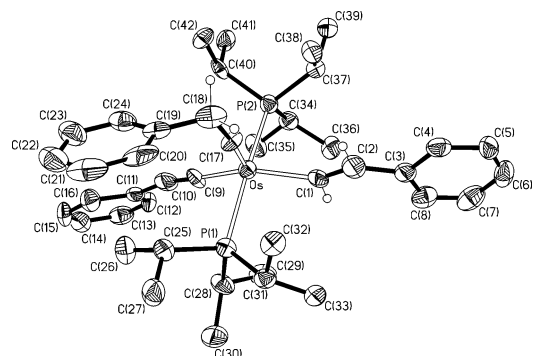


Figure 1. Molecular diagram of the cation of complex **2**.

Chart 1

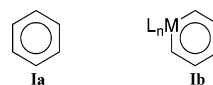
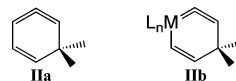
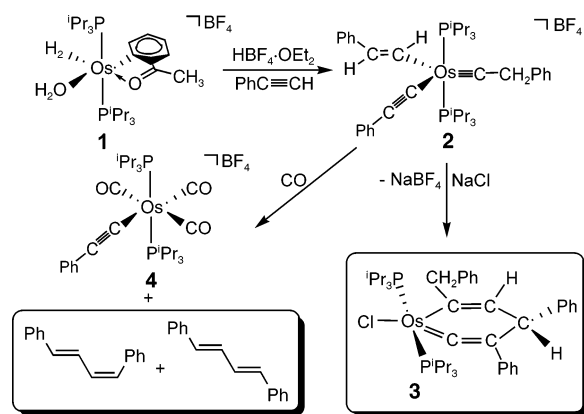


Chart 2



Scheme 1



1.525(7), and 1.532(6) Å in *S*). These values strongly support the metalla-**IIb** structure. In contrast to the C_1 -symmetric structure of 1,2,4-cyclohexatriene, the six-membered ring in **3** is almost planar. The torsion angle C(18)–C(17)–C(24)–Os(1) (C(60)–C(59)–C(66)–Os(2) in *S*) is 165.0(8)° (–162.7(8)° in *S*). The greater size of the osmium atom with regard to the carbon atom is manifested in the C(17)–C(24)–Os(1) angle (C(59)–C(66)–Os(2) in *S*). Its value of 158.5(3)° (159.3(4)° in *S*) is about 28° larger than the related parameter (C(1)–C(2)–C(3) angle) calculated for the isobenzene (130.8°^{5d} or 132.4°^{7b}). This angle is also slightly larger than the Os–C(sp)–C(sp²) angle in the osmabenzene complexes reported by Jia and co-workers (148.7(3)° and 153.8(4)°).¹² In the

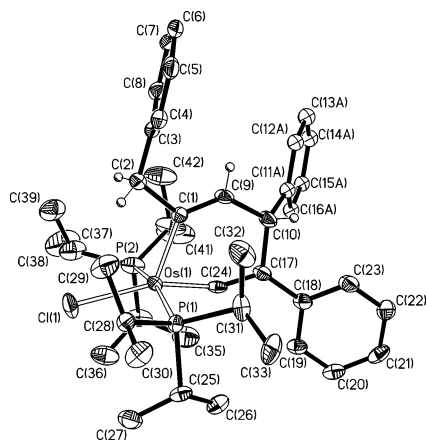
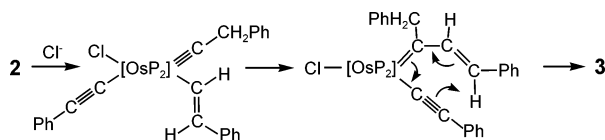


Figure 2. Molecular diagram of complex 3.

Scheme 2



$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum at $-40\text{ }^\circ\text{C}$ in dichloromethane- d_2 , the carbon atoms of the six-membered ring display resonances at 289.3 (C(24)), 135.8 (C(1)), 124.0 (C(9)), 103.1 (C(17)), and 39.0 (C(10)) ppm. As a result of the chirality of the sp^3 -carbon atom C(10), the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows an AB spin system centered at 11.2 ppm ($\Delta\nu = 583\text{ Hz}$, $J_{\text{AB}} = 293\text{ Hz}$). This spectrum is consistent with the geometry around the osmium atom, which can be described as that of **2** with angles within the Y-shaped equatorial plane of $77.89(17)^\circ$ (C(24)–Os(1)–C(1)), $162.28(13)^\circ$ (C(24)–Os(1)–Cl(1)), and $119.75(12)^\circ$ (C(1)–Os(1)–Cl(1)) in enantiomer *R*, and $77.79(19)^\circ$ (C(66)–Os(2)–C(43)), $154.90(13)^\circ$ (C(66)–Os(2)–Cl(2)), and $128.30(15)^\circ$ (C(43)–Os(2)–Cl(2)) in enantiomer *S*.

Complex **3**, which was isolated as a lilac solid in 64% yield, is the result of the coordination of a chloride ligand to the osmium atom of **2** and the migration of the alkenyl group from the metallic center to both the alkenyl and the carbyne ligands. The addition is specific: the C_α atom of the alkenyl group is coupled with the C_α atom of the carbyne, while the C_β atom of the alkenyl is coupled with the C_β atom of the alkyne. This double coupling could be rationalized according to Scheme 2. The coordination of chloride to the osmium atom promotes the migration of the alkenyl group onto the C_α atom of the carbyne followed by a ring-closure of the resulting alkenyl-alkenylcarbene-substituted intermediate.

In contrast to chloride, CO only promotes the coupling between the alkenyl group and the carbyne ligand. Under a carbon monoxide atmosphere, complex **2** affords *cis,trans*- and *trans,trans*-1,4-diphenylbutadiene (1:1.5 molar ratio) and the alkenyl-tricarbonyl derivative **4**.¹³ This single coupling also involves an alkenyl-alkenylcarbene intermediate. However, in this case, the alkenyl-carbene ligand undergoes the destabilization produced by a carbonyl group *trans*-disposed. Thus, before the coupling with the alkenyl group, it evolves into the butadienes by a 1,2-hydrogen shift from the CH_2Ph substituent to the C_α atom.

The difference in behavior between these alkenyl-alkenylcarbene intermediates is in agreement with the difference in behavior previously observed for the butadienyl compounds $\text{Os}\{(\text{E})\text{-CH}=\text{CHC}(\text{CH}_3)=\text{CH}_2\}(\kappa^2\text{-O}_2\text{CCH}_3)(\text{CO})(\text{P}^i\text{Pr}_3)_2$ and $\text{Os}\{(\text{Z})\text{-CH}=\text{CHC}(\text{CH}_3)=\text{CH}_2\}\{\kappa^1\text{-OC}(\text{O})\text{CH}_3\}(\text{CO})_2(\text{P}^i\text{Pr}_3)_2$. The first one, with a π -donor ligand *trans*-disposed to the butadienyl, reacts with HBF_4 to give the alkenylcarbene derivative $[\text{Os}\{\text{=CHCH}=\text{C}(\text{CH}_3)_2\}(\kappa^2\text{-}$

$\text{O}_2\text{CCH}_3)(\text{CO})(\text{P}^i\text{Pr}_3)_2]\text{BF}_4$. On the other hand, complex $\text{Os}\{(\text{Z})\text{-CH}=\text{CHC}(\text{CH}_3)=\text{CH}_2\}\{\kappa^1\text{-OC}(\text{O})\text{CH}_3\}(\text{CO})_2(\text{P}^i\text{Pr}_3)_2$, which has a carbonyl group *trans*-disposed to the butadienyl, reacts with HBF_4 to afford isoprene and *cis*- $[\text{Os}(\kappa^2\text{-O}_2\text{CCH}_3)(\text{CO})_2(\text{P}^i\text{Pr}_3)_2]\text{BF}_4$.¹⁴

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Supporting Information Available: Experimental details for the synthesis for **2–4** as well as crystal structure determinations, including bond lengths and angles of compounds **2** and **3** (PDF and CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- When the reaction is carried out in the absence of acid, a mixture containing the hydride-vinylidene- π -alkyne complex $[\text{OsH}(\text{=C}=\text{CHPh})(\eta^2\text{-HC}=\text{CPh})(\text{P}^i\text{Pr}_3)]\text{BF}_4$ and a hydride-metallacyclopropene compound is obtained (see: Barrio, P.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2003**, *22*, 2472). In the presence of 1.2 equiv of $\text{HBF}_4\cdot\text{OEt}_2$, the reaction leads to a mixture of **3** and the above-mentioned derivatives.
- Osmium complexes containing η^1 -carbon ligands are almost invariably saturated and resist becoming unsaturated, and the presence of at least one π -donor ligand makes such unsaturated species achievable (see for example: Esteruelas, M. A.; Oro, L. A. *Adv. Organomet. Chem.* **2001**, *47*, 1). Complex **2** is a rare case of unsaturated osmium compound of this type that does not have any π -donor ligand.
- Complex **3** is also the first cyclic metallaallene compound. For reviews of metallaallenes see: (a) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197. (b) Bruce, M. I. *Chem. Rev.* **1998**, *98*, 2797. (c) Puerta, M. C.; Valerga, P. *Coord. Chem. Rev.* **1999**, *193–195*, 977. (d) Cadierno, V.; Gamasa, M. P.; Gimeno, J. *Eur. J. Inorg. Chem.* **2001**, 571.
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- Complex **4** was isolated as a white solid in 64% yield. Selected spectroscopic data: IR (KBr, cm^{-1}), $\nu(\text{C}=\text{C})$ 2115 (m), $\nu(\text{CO})$ 2036 (s) and 1989 (s); $^{31}\text{P}\{^1\text{H}\}$ NMR (121.42 MHz, CD_2Cl_2 , 293 K) δ 13.6(s); $^{13}\text{C}\{^1\text{H}\}$ (75.42 MHz, CD_2Cl_2 , 223 K, plus APT) δ 175.5 (t, $J_{\text{P-C}} = 8.7\text{ Hz}$, mutually *trans* CO groups), 174.1 (t, $J_{\text{P-C}} = 6.0\text{ Hz}$, CO), 114.5 (t, $J_{\text{P-C}} = 2.3\text{ Hz}$, CPh), 73.1 (t, $J_{\text{P-C}} = 12.9\text{ Hz}$, $\text{OsC}\equiv$).
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