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Isomerization of $\mathrm{CH_3C{\equiv}CPh}$ to Phenylallene Promoted by an Osmium Hydride Complex

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Summary: Treatment of $\mathit{OsH_3Cl(PPh_3)_3}$ *in benzene with excess* $\mathit{CH_3C{\equiv}CPh}$ *produced cis-*$\mathit{CH_3CH{=}CHPh}$ *and the novel complex* $\mathit{OsCl(C(CH_3){=}CHPh)(CH_2{=}C{=}CHPh)(PPh_3)_2}$*, which contains a β-agostic vinyl ligand and a phenylallene ligand. The structure of the latter unusual complex has been confirmed by a single-crystal X-ray diffraction study.*

Terminal alkynes $\mathrm{HC{\equiv}CR}$ are thermodynamically more stable than their vinylidene forms $\mathrm{:C{=}CHR}$. However, many coordinatively unsaturated transition-metal complexes $\mathrm{L}_n\mathrm{M}$ readily react with $\mathrm{RC{\equiv}CH}$ to give vinylidene complexes $\mathrm{L}_n\mathrm{M{=}C{=}CHR}$ rather than η^2-alkyne complexes $\mathrm{L}_n\mathrm{M}(\eta^2\text{-}\mathrm{HC{\equiv}CR})$.[1] Repulsive interaction of an alkyne π orbital with a filled metal d orbital in $\mathrm{L}_n\mathrm{M}(\eta^2\text{-}\mathrm{HC{\equiv}CR})$ renders these complexes less stable relative to the corresponding vinylidene complexes $\mathrm{L}_n\mathrm{M{=}C{=}CHR}$.[2] The repulsive interaction should also occur with internal alkynes $\mathrm{R_2CHC{\equiv}CR'}$, and thus $\mathrm{R_2CHC{\equiv}CR'}$ may isomerize to $\mathrm{R_2C{=}C{=}CHR'}$ on complexation to certain transition-metal fragments. Isomerization of alkynes to allenes is interesting because allenes are useful precursors for organic synthesis,[3] and because the transformation may be involved in organometallic synthesis.[4−6] However, only a few reports on metal-mediated isomerization of internal alkynes to allenes have appeared, although examples of metal-mediated isomerization of terminal alkynes to vinylidene are numerous.[1] Formation of allene complexes has been reported in the reactions of $\mathrm{ReCl(N_2)(dppe)_2}$[7] and $\mathrm{RhCl(C_2H_4)(As(\mathit{i}\text{-}Pr)_3)_2}$[8] with internal alkynes. Acid-, silica-, and alumina-promoted isomerization of preformed alkyne complexes, such as $(\eta^5\text{-}\mathrm{MeC_5H_4})\mathrm{Mn}(\eta^2\text{-}\mathrm{RC{\equiv}CR'})$ (basic alumina oxide),[9] $\mathrm{CpRh(MeC{\equiv}CMe)(P(\mathit{i}\text{-}Pr)_3)}$ (alumina),[5] $\mathrm{Cp^*Re(CO)_2(MeC{\equiv}CMe)}$ (trifluoroacetic acid),[10] and $\mathrm{CpMn(CO)_2(cyclooctyne)}$ (silica, basic and acidic alumina)[11] to allene complexes has been reported.

In acid-promoted isomerization of alkyne complexes to allene complexes, 1-metallacyclopropene[10] or η^1-vinyl species[5] have been suggested as the key intermediates, which may be formed by direct protonation of an alkyne ligand[10] or from the insertion reaction of an intermediate hydrido alkyne complex.[5] In this regard, it would be interesting to demonstrate that preformed hydride complexes could also react with internal alkynes to give allene complexes. During the investigation of the reactivity of $\mathrm{OsH_3Cl(PPh_3)_3}$[12] with alkynes, we have discovered that the unusual complex $\mathrm{OsCl(C(CH_3){=}CHPh)(CH_2{=}C{=}CHPh)(PPh_3)_2}$ is produced from the reaction of $\mathrm{CH_3C{\equiv}CPh}$ with $\mathrm{OsH_3Cl(PPh_3)_3}$. The transformation appears to be the first example of reactions of preformed hydride complexes with internal alkynes to give well-defined allene complexes.

Treatment of $\mathrm{OsH_3Cl(PPh_3)_3}$ (**1**) in benzene with excess $\mathrm{CH_3C{\equiv}CPh}$ at room temperature produced $\mathrm{OsCl(C(CH_3){=}CHPh)(CH_2{=}C{=}CHPh)(PPh_3)_2}$ (**2**) along with the hydrogenated product *cis*-$\mathrm{CH_3CH{=}CHPh}$ (Scheme 1).[13] Compound **2** could also be obtained by reacting $\mathrm{OsHCl(PPh_3)_3}$[12] with excess $\mathrm{CH_3C{\equiv}CPh}$ at room temperature. The structure of **2** has been confirmed by a single-crystal X-ray diffraction study (Figure 1).[14] It reveals that two molecules of $\mathrm{PhC{\equiv}CCH_3}$ have been incorporated into the osmium center: one in the form of the vinyl group $\mathrm{PhCH{=}CCH_3}$ and the other one in the form of the phenylallene ligand $\mathrm{PhCH{=}C{=}CH_2}$. Compound **2** represents the first structurally characterized mononuclear osmium allene complex. Another

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(13) Preparation of **2**. To a suspension of $\mathrm{OsH_3Cl(PPh_3)_3}$ (0.40 g, 0.39 mmol) in benzene (30 mL) was added $\mathrm{CH_3C{\equiv}CPh}$ (0.25 mL, 1.97 mmol). The reaction mixture was stirred at room temperature for 8 h to give a brown solution. The solvent was pumped away under vacuum, and the residue was redissolved in a minimum amount of $\mathrm{CH_2Cl_2}$ (~2 mL). A brownish yellow solid was formed when methanol (30 mL) was slowly added to the residue. The solid was collected by filtration, washed with methanol (2 × 20 mL) and hexane (2 × 20 mL), and dried under vacuum overnight. Yield: 0.24 g, 63.1%. Anal. Calcd for $\mathrm{C_{54}H_{47}ClP_2Os}$: C, 65.94; H, 4.82. Found: C, 65.36; H, 5.12. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (121.5 MHz, $\mathrm{CDCl_3}$): δ −6.3 (s). ^{1}H NMR (300.13 MHz, $\mathrm{CDCl_3}$): δ 0.06 (br, 3 H, $\mathrm{OsC(C\mathit{H}_3){=}C}$), 1.27 (br, 2 H, $\mathrm{C\mathit{H}_2{=}C{=}C}$), 5.41 (br, 1 H, $\mathrm{OsC(CH_3){=}C\mathit{H}Ph}$), 6.59 (br, 1 H, $\mathrm{CH_2{=}C{=}C\mathit{H}Ph}$), 7.72~7.07 (m, 40 H, Ph, $\mathrm{PPh_3}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (100.40 MHz, $\mathrm{CD_2Cl_2}$): 155.06 (t, J(PC) = 6.19 Hz, $\mathrm{Os}(\eta^2\text{-}\mathrm{CH_2{=}\mathit{C}{=}CHPh})$), 154.13 (t, J(PC) = 6.26 Hz, $\mathrm{Os{-}\mathit{C}(CH_3){=}C}$), 140.93−124.67 (m, Ph, $\mathrm{PPh_3}$), 122.99 (s, $\mathrm{OsC(CH_3){=}\mathit{C}HPh}$), 119.86 (s, $\mathrm{Os}(\eta^2\text{-}\mathrm{CH_2{=}C{=}\mathit{C}HPh})$), 8.31 (s, $\mathrm{Os}(\eta^2\text{-}\mathit{C}\mathrm{H_2{=}C{=}C})$), 3.47 (s, $\mathrm{OsC(\mathit{C}H_3){=}CHPh}$).

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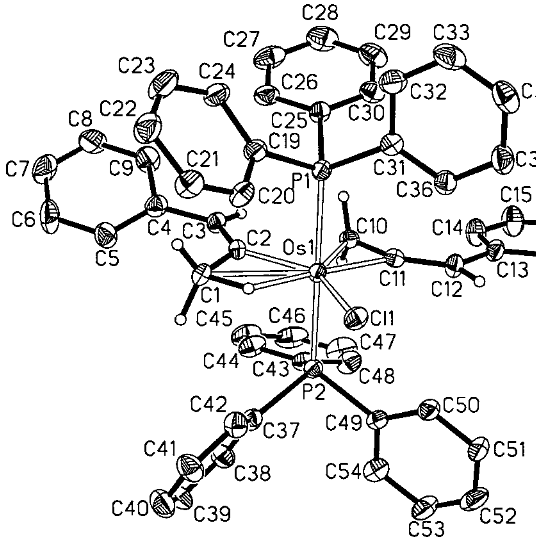
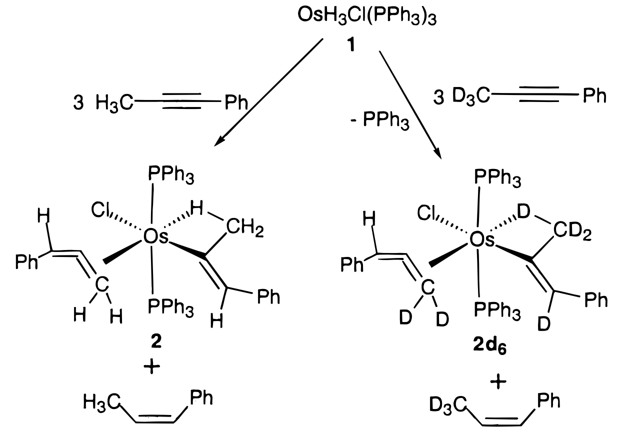


Figure 1. Molecular structure for OsCl(C(CH$_3$)=CHPh)(CH$_2$=C=CHPh)(PPh$_3$)$_2$. The thermal ellipsoids are drawn at the 40% probability level. Solvent molecules and the hydrogen atoms of the phenyl rings are omitted for clarity. Selected bond distances (Å) and angles (deg) are as follows: Os(1)−P(1), 2.3934(17); Os(1)−P(2), 2.3906(16); Os(1)−Cl(1), 2.4481(16); Os(1)−H(1A), 1.8110; Os(1)−C(1), 2.527(6); Os(1)−C(2), 2.023(6); Os(1)−C(10), 2.119(6); Os(1)−C(11), 1.993(6); C(1)−C(2), 1.519(8); C(2)−C(3), 1.314(8); C(10)−C(11), 1.389(8); C(11)−C(12), 1.347(8); P(1)−Os(1)−P(2), 179.66(6); P(1)−Os(1)−Cl(1), 89.86(6); P(2)−Os(1)−Cl(1), 90.47(6); P(1)−Os(1)−C(1), 89.75(14); P(2)−Os(1)−C(1), 90.16(14); P(1)−Os(1)−C(2), 88.30(17); P(2)−Os(1)−C(2), 91.43(17); C(1)−Os(1)−C(2), 36.9(2); C(10)−Os(1)−P(1), 90.02(16), C(10)−Os(1)−P(2), 89.74(16); C(11)−Os(1)−P(1), 90.45(16); C(11)−Os(1)−P(2), 89.52(16); C(10)−Os(1)−C(11), 39.3(2); C(1)−Os(1)−C(10), 119.0(2); C(2)−Os(1)−C(10), 82.1(2); C(1)−Os(1)−C(11), 158.3(2); C(2)−Os(1)−C(11), 121.4(2); C(1)−Os(1)−Cl(1), 100.13(16); C(2)−Os(1)−Cl(1), 137.02(18); C(10)−Os(1)−Cl(1), 140.89(18); C(11)−Os(1)−Cl(1), 101.56(17); C(1)−C(2)−C(3), 128.0(6); C(10)−C(11)−C(12), 141.7(6).

Scheme 1



interesting feature of the structure is that there exists an agostic interaction between the osmium center and one of the protons of the CH$_3$ group of the vinyl ligand. β-Agostic vinyl complexes are interesting, as they can be regarded as the resting states for the interconversion of allene and vinyl complexes.[15,16] Well-characterized β-agostic vinyl complexes are still rare,[17] although β-agostic alkyl complexes are numerous.[18]

Consistent with the solid structure, the ^{31}P{^{1}H} NMR spectrum of **2** in CDCl$_3$ showed a singlet at −6.3 ppm. In the ^{1}H NMR spectrum, the allene proton signals were observed at 1.27 (CH$_2$) and 6.59 (=CHPh) ppm; the vinyl proton signal was observed at 5.41 ppm. The methyl proton signal was observed at 0.06 ppm. The chemical shift is unusually upfield for typical CH$_3$ attached to an sp^2-hybridized carbon but is consistent with the presence of an agostic interaction. For comparison, the signal of the methyl group with an agostic interaction in [IrPh(C(CH=CHCMe$_3$)=CHCMe$_3$)(PMe$_3$)$_3$]PF$_6$ was observed at −0.7 ppm.[19] Consistent with the existence of the agostic interaction in **2**, the ^{13}C NMR spectrum showed the CH$_3$ signal at 3.47 ppm. For comparison, the signal of the methyl group with an agostic interaction in Cp*Ru(C(*Me*)=C(Me)C≡CCMe$_3$)(PPh$_3$) was observed at 4.5 ppm.[17]

We have monitored the reaction at low temperature by ^{31}P{^{1}H} and ^{1}H NMR in order to detect the intermediates for the formation of complex **2** from the reaction of OsH$_3$Cl(PPh$_3$)$_3$ with 3.5 equiv of CH$_3$C≡CPh. Below −13 °C in CD$_2$Cl$_2$, no appreciable reaction was observed. At −8 °C, a new ^{31}P signal at 16.9 ppm started to appear along with that of free PPh$_3$. The ^{1}H NMR spectrum of the newly formed osmium complex showed a vinyl signal at 5.44 ppm and a CH$_3$ signal at −0.88 ppm. Again, the chemical shift of the methyl group is unusually upfield for typical CH$_3$, implying the presence of an agostic interaction. The ^{1}H NMR spectrum of the newly formed osmium complex also showed two triplet hydride signals (each integrated to one proton relative to the vinyl signal) at −9.16 (J(PH) = 15.0 Hz) and −11.61 (J(PH) = 15.0 Hz) ppm, indicating that the complex only contains two PPh$_3$ ligands. The spectroscopic data are consistent with the formation of OsClH$_2$(H$_3$CC=CHPh)(PPh$_3$)$_2$ (**3**). When the temperature was increased to −1 °C, ^{1}H signals due to compound **2**, *cis*-CH$_3$CH=CHPh, and OsHCl(PPh$_3$)$_3$ appeared. At this temperature, a minor singlet ^{31}P{^{1}H} peak at 19.0 ppm could also be seen. After the reaction temperature was raised to room temperature and the reaction mixture was allowed to stand for 30 min, the signals of complex **1** and **3** disappeared and the only detectable species were OsHCl(PPh$_3$)$_3$ (major), PPh$_3$, *cis*-CH$_3$CH=CHPh, complex **2** (minor), and a very minor

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(14) Crystallographic details for **2** are as follows. Crystallographic data for **2**·2C$_6$H$_6$: triclinic, space group $P\bar{1}$ (No. 2), a = 13.4250(18) Å, b = 14.6549(1) Å, c = 15.1240(19) Å, α = 84.868(3)°, β = 88.023(3)°, γ = 68.142(3)°, V = 2750.5(6) Å^3, Z = 2, D_{calcd} = 1.376 g cm^{-3}, Mo Kα radiation (λ = 0.710 73 Å), μ = 24.65 cm^{-1}, crystal size 0.18 × 0.08 × 0.08 mm^3. Of 18 650 reflections collected (Bruker SMART CCD area detector, 294 K), 12 484 were unique and 7560 were observed with $I > 2\sigma(I)$. The structure was solved by direct methods and refined by full-matrix least squares on F^2 using the Bruker SHELXTL (version 5.10) program package. All non-hydrogen atoms were refined anisotropically. The H atoms, except those for the phenyl rings, were located from the difference Fourier map and were constrained to ride on the respective carbon after several cycles of refinement. The H atoms for all phenyl rings were introduced at calculated positions and refined via a riding model. The structure converged at R_F = 0.0543 and R_{wF^2} = 0.1120 (for all data).

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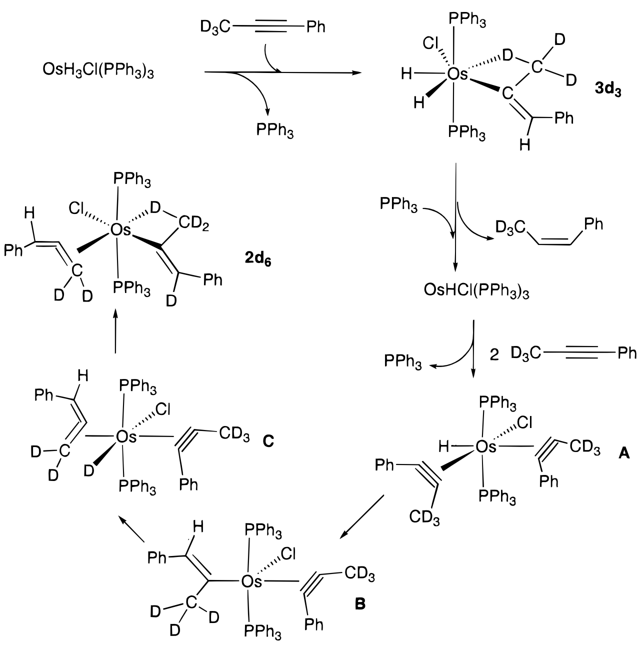
Scheme 2



amount of an unknown species having a ^{31}P signal at 19.0 ppm. $OsHCl(PPh_3)_3$ was completely converted to compound **2** when the reaction mixture was allowed to stand at room temperature for 8 h.

To further understand the mechanism for the formation of complex **2**, we have reacted $OsH_3Cl(PPh_3)_3$ with $CD_3C{\equiv}CPh$ under similar conditions. ^2H NMR of the isolated product shows that $OsCl(C(CD_3){=}CDPh)(CD_2{=}C{=}CHPh)(PPh_3)_2$ was formed exclusively (see Scheme 1).[20] The results strongly suggest that the allene ligand is not formed by a simple 1,3-hydrogen shift and that the vinyl ligand is not formed by simple insertion of $CH_3C{\equiv}CPh$ into an Os−H bond.

A plausible sequence for the formation of complex **2** is illustrated in Scheme 2 using $D_3CC{\equiv}CPh$ as the substrate. Reaction of $OsH_3Cl(PPh_3)_3$ with the first equivalent of $D_3CC{\equiv}CPh$ gives $OsHCl(PPh_3)_3$ and *cis*-$CD_3CH{=}CHPh$ through intermediate **$3d_3$**, which has been detected by $^{31}P\{^1H\}$ and ^1H NMR at low temperature. $OsHCl(PPh_3)_3$ can then react with additional $D_3CC{\equiv}CPh$ to give the bis(alkyne) intermediate **A**. Formation of **A** is reasonable, as reaction of $OsH_3Cl(PPh_3)_3$ with excess ethylene gives ethane and $OsHCl(CH_2{=}CH_2)_2(PPh_3)_2$.[12] Intermediate **A** undergoes an insertion reaction to give the vinyl complex **B**.[21] Oxidative addition of one of the C−D bonds of the vinyl group in **B** would produce the deuteride complex **C**, which then undergoes another insertion reaction to give the final product **$2d_6$**. Although the hydride and vinyl intermediates have not been detected, similar reaction sequences have been proposed for the formation of $RhCl(CH_2{=}C{=}CH_2)(As(i\text{-}Pr)_3)_2$ from the reaction of $RhCl(C_2H_4)(As(i\text{-}Pr)_3)_2$ with $HC{\equiv}CMe$[8] and for the formation of $[CpRh(\eta^3\text{-}CH_3CHCHCH_2)(P(i\text{-}Pr)_3)]^+$ from protonation of $CpRh(MeC{\equiv}CMe)(P(i\text{-}Pr)_3)$.[5] A related reaction mechanism has been proposed for the reaction of $Os(CD_2Ph)(C{\equiv}CPh)(CO)_2(P(i\text{-}Pr)_3)_2$ with HBF_4 to give $[Os(\eta^3\text{-}PhCHCDCDPh)(CO)_2(P(i\text{-}Pr)_3)_2]BF_4$.[22] It should be noted that 1-metallacyclopropene rather than a η^1-vinyl species is involved in the formation of $[Cp^*Re(CO)_2(\eta^3\text{-}CH_3CHCHCH_2)]^+$ from protonation of $Cp^*Re(CO)_2(MeC{\equiv}CMe)$[6] and in the formation of $Cp^*Re(CO)_2(CH_2{=}C{=}CMe)$ from acid-catalyzed isomerization of $Cp^*Re(CO)_2(MeC{\equiv}CMe)$.[10] In the latter case, the allene ligand is more likely formed by direct deprotonation of metallacyclopropene rather than β-hydrogen elimination.

In summary, we have shown that reaction of $CH_3C{\equiv}CPh$ with $OsH_3Cl(PPh_3)_3$ produced the unusual complex $OsCl(C(CH_3){=}CHPh)(CH_2{=}C{=}CHPh)(PPh_3)_2$, which contains a β-agostic vinyl ligand and a phenylallene ligand. The vinyl complex formed by insertion of $H_3C{\equiv}CPh$ into a Os−H bond appears to be the key intermediate for the formation of the allene ligand. Structurally characterized β-agostic vinyl ligands are interesting, as related species may be involved in the interconversion of allene and vinyl complexes. We are currently exploring the scope and uses of the interesting reactions.

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Supporting Information Available: Tables of crystallographic details, bond distances and angles, atomic coordinates and equivalent isotropic displacement coefficients, and anisotropic displacement coefficients for $OsCl(C(CH_3){=}CHPh)(CH_2{=}C{=}CHPh)(PPh_3)_2{\cdot}2C_6H_6$. The material is available free of charge via the Internet at http://pubs.acs.org.

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(20) $OsCl(C(CD_3){=}CDPh)(CD_2{=}C{=}CHPh)(PPh_3)_2$ (**$2d_6$**) was prepared by the same procedure, with the use of $CD_3C{\equiv}CPh$ instead of $CH_3C{\equiv}CPh$. $CD_3C{\equiv}CPh$ was prepared by addition of CD_3I in THF at dry ice/acetone temperature to a freshly prepared solution of lithium phenylacetylide in THF and hexane (1:1). The $LiC{\equiv}CPh$ was in turn prepared by adding phenylacetylene to a fresh solution of butyllithium in hexane and THF (1:1) at 0 °C. Selected characterization data for **$2d_6$**: $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$) δ −6.13 (s); ^1H NMR (399.65 MHz, $CDCl_3$) δ 6.36 (br, 1H, $CD_2{=}C{=}CHPh$), 7.50~6.83 (m, 40 H, Ph, PPh_3); ^2H NMR (61.25 MHz, $CHCl_3$) δ −0.11 (br, 3 D, $OsC(CD_3){=}CDPh$), 1.11 (br, 2 D, $Os(\eta^2\text{-}CD_2{=}C{=}CHPh)$, 5.31 (br, 1D, $OsC(CD_3){=}CDPh$).

(21) For recent examples of insertion of alkynes into an Os−H bond, see for example: (a) Oliván, M.; Clot, E.; Eisenstein, O.; Caulton, K. G. *Organometallics* **1998**, *17*, 3091. (b) Huang, D.; Oliván, M.; Huffman, J. C.; Eisenstein, O.; Caulton, K. G. *Organometallics* **1998**, *17*, 4700. (c) Buil, M. L.; Esteruelas, M. A. *Organometallics* **1999,** *18*, 1798. (d) Bohanna, C.; Callejas, B.; Edwards, A. J.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Ruiz, N.; Valero, C. *Organometallics* **1998**, *17*, 373 and references therein. (e) Esteruelas, M. A.; Oro, L. A.; Valero, C. *Organometallics* **1995**, *14*, 3596.

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