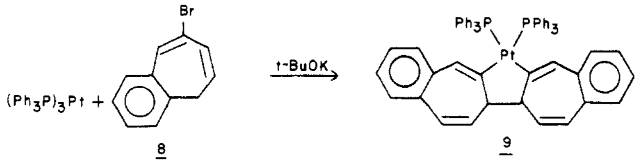
localized between C1–C7, C3–C4, and C5–C6.

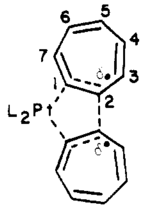
A reasonable pathway for formation of **7** is given in Scheme I. In this we propose dehydrobromination of **3** to give cycloheptatetraene which is trapped by **2** to give a $\pi$-complex which then reacts with a second equivalent of the allene to give the dimer.[4a,b]

The anomalous behavior of **4** and the allene from **8** is probably due in part to relief of ring strain which should accelerate both formation of the bis adduct **6** and closure to the metallocyclopentane **7**. However, it would appear that relief of strain alone is not sufficient to cause dimerization since reaction of 1,2-cycloheptadiene with either $(Ph_3P)_2Pt(ethylene)$[7] or $(Ph_3P)_3Pt$ gave only the allene complex; the latter even in the presence of a large excess of the allene.



Conjugation in cycloheptatetraene should also favor the dimerization by stabilizing **6**. MO calculations show that, relative to unstrained allenes, the HOMO of cycloheptatetraene is raised and its LUMO is lowered. Both should favor $\pi$-bond formation to Pt(0).

The regiochemistry of dimerization of **4** and the allene from **8** is also anomalous in that it is opposite to that normally found in allene dimerizations induced by group 8 metals.[8] Hoffmann has addressed the regiochemistry question for metal-induced dimerizations of alkenes and has suggested that it is usually dominated by the magnitude of the LUMO coefficients of the uncomplexes olefin (which, in turn, influences the HOMO coefficients in the complex).[9] Application of this theory to cycloheptatetraene dimerization predicts exactly the opposite regiochemistry from that observed. For cycloheptatetraene we therefore suggest that the dimerization step may have significant diradical character as in **10** and that stabilization of the incipient radical by conjugation with the double bonds dictates the regiochemistry and also accelerates the ring closure.[10]



**10**

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**Registry No.** 7, 97719-83-0; 8, 97719-86-3; 9, 97719-84-1; i, 97719-85-2; $(Ph_3P)_3Pt$, 13517-35-6; bromocycloheptatriene, 32743-67-2.

**Supplementary Material Available:** Tables of distances and bond angles, final positional parameters, and structure factors (31 pages). Ordering information is given on any current masthead page.

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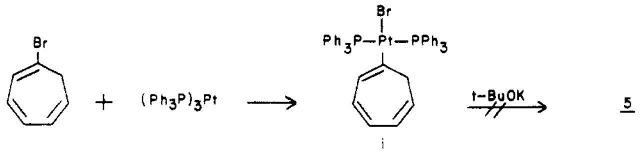
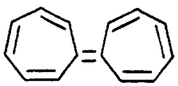
(4) (a) In principle, insertion to form **i** could occur which could then undergo elimination to give **5**.



However, **i**,[5] synthesized in a separate reaction, was found to be inert to *t*-BuOK under the above conditions. Also, implicit in this scheme is the assumption that dimerization occurs after complexation. Consistent with this is our finding the heptafulvalene **ii** is inert to **2**.[6] (b) **Note Added**



**ii**

**in Proof**: The $\pi$-complex **5** has now been isolated, characterized, and found to react with a second mole of **4** to give **7**.

(5) **i**: mp 216.0–216.5 dec; IR (KBr) 3050 w, 3010 w, 1571 w, 1505 m, 1480 m, 1430 s, 1385 m, 1180 m, 1100 s, 1030 m, 1000 m, 750 m, 700 s, 500 s, cm$^{-1}$; $^1$H NMR (100 MHz, $CDCl_3$) $\delta$ 2.23 (td, $^3J_{PtH}$ = 39 Hz, $J_{HH}$ = 7.1 Hz, H7), 4.30 (dt, $J$ = 6.84 Hz, $J$ = 6.0 Hz, 1 H), 5.6 (t, $J_{PtH}$ = 32 Hz, 1 H), 5.64 (s, 2 H), 6.0 (s, 3 H), 7.2 ($Ph_3P$, 18 H), 7.7 ($Ph_3P$, 12 H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 80.5 (C7), 115.4, 122.9, 124.58, 127.70 (t, $^3J_{PC}$ = 5.27 Hz, $Ph_3P$, meta), 130.1 (s, $Ph_3P$, para), 131.0 (t, $^2J_{PtC}$ = 46 Hz, $Ph_3P$, ipso), 14.3, 134.45, 135.2 (m, $Ph_3P$, ortho), 139.4 (C1); $^{31}$P NMR ( 121.5 MHz, $CDCl_3$) $\delta$ 21.34 (t, $^1J_{HP}$ = 3215 Hz). Anal. Calcd for $C_{43}H_{37}Br_1P_2Pt_1$: C, 57.94; H, 4.15. Found: C, 57.76, H, 4.23.

(6) Cycloheptatetraene is known to dimerize to heptafulvalene. Waali, E. E.; Jones, W. M. *J. Org. Chem.* **1973**, *38*, 2573 and references cited therein.

(7) Visser, J. P.; Ramakers, J. E. *J. Chem. Soc., Chem. Commun.* **1972**, 178.

(8) (a) Ingrosso, G.; Immirizi, A.; Parri, L. *J. Organomet. Chem.* **1973**, *60*, c35. (b) Jolly, P. W.; Kruger, C.; Salz, R.; Skeutowski, J. C. *J. Organomet. Chem.* **1979**, *165*, c39.

(9) McKinney, R. J.; Thorn, D. L.; Hoffmann, R.; Stockis, A. *J. Am. Chem. Soc.* **1981**, *103*, 2595.

(10) If simple allene dimerization is also diradicaloid in nature, the observed regiochemistry (which is opposite to **7** and **9**) would be expected since radicals typically add to the allene terminal carbon to give carbon vinyl radicals that are more stable than the perpendicular allyl radicals that would be formed from attack at the central carbon.

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# Intramolecular Coupling of $\eta^2$-Iminoacyl Functions at Group 4 Metal Centers

**Stanley L. Latesky, Anne K. McMullen,
Gerald P. Niccolai, and Ian P. Rothwell***

*Department of Chemistry, Purdue University
West Lafayette, Indiana 47907*

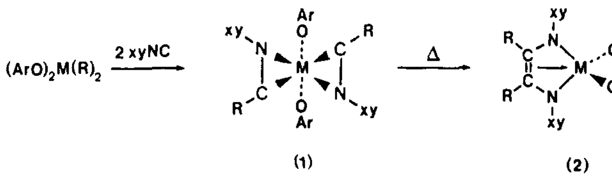
**John C. Huffman**

*Molecular Structure Center, Indiana University
Bloomington, Indiana 47405*

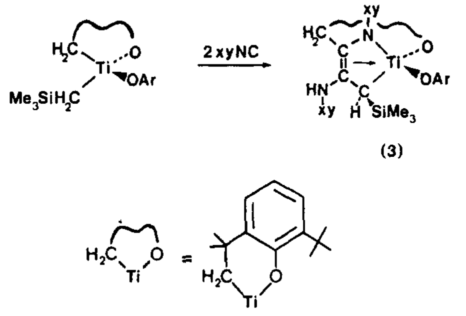
*Received May 8, 1985*

*Summary:* The intramolecular cis coupling of $\eta^2$-iminoacyl groups at Ti(IV) and Zr(IV) metal centers to produce chelating enediamide ligands has been shown to be facile. Evidence that coupled products can also be formed containing a trans arrangement of nitrogen atoms has also been obtained.

Scheme I



(a). M = Ti; OAr = 2,6-di-isopropylphenoxide; R = $CH_2Ph$.
(b). M = Zr; OAr = 2,6-di-tert-butylphenoxide; R = $CH_3$.



A unique reactivity associated with high valent lanthanide,[1] actinide,[2] and early-transition-metal[3] acyl and related formyl functions is their coupling, either inter- or intramolecularly, to produce enediolate ligands. However, in no case has a discrete bis(acyl) precursor been isolated prior to coupling. We have recently shown that with suitable aryl oxide ligation it is possible to observe a facile coupling of acyl and iminoacyl groups at zirconium metal centers.[4] We wish to report here the first observed coupling of $\eta^2$-iminoacyl groups and furthermore the observation that products can result both from cis and trans coupling.

The complexes $Zr(OAr')_2Me_2$ and $Ti(OAr'')_2(CH_2Ph)_2$ (OAr′ = 2,6-di-*tert*-butyl, OAr″ = 2,6-diisopropylphenoxide)[5] will smoothly insert 2 equiv of 2,6-dimethylphenyl isocyanide (xyNC) to give the corresponding bis($\eta^2$-iminoacyl) complexes 1 (Scheme I).[6] All data on these two compounds is consistent with a structure analogous to that characterized for $Zr(OAr')_2(Bu\text{-}t\text{-}NCCH_2Ph)_2$.[4] On thermolysis (120 °C/toluene) an essentially quantitative coupling of the $\eta^2$-iminoacyl groups occurs to produce a chelated enediamide ligand (a doubly reduced 1,4-diaza-1,3-butadiene fragment).[7] The nonplanar geometry of the diazametallocyclopentene ring is indicated by the temperature dependence of the $^1H$ NMR spectrum for both complexes (**2a**,**b**). Below −10 °C nonequivalent aryl oxide ligands are observed with two types of xylyl methyl resonances. Furthermore an AB pattern is present for the benzyl methylene groups of **2a**. At higher temperatures facile exchange of these nonequivalent groups occurs, consistent with a process whereby "inversion" of the $\sigma^2,\pi$-coordinated enediamide through a planar coordination mode takes place. Similar fluxionality has been noted for group 4 metal butadiene derivatives.[8] The value of this inversion barrier $\Delta G^{\ddagger}$ has been estimated from coalescence temperatures ($T_c$) as 15.1 (±0.5) kcal mol⁻¹ (40 °C) for **2a** and 14.5 (±0.5) kcal mol⁻¹ (0 °C) for **2b**. Analysis of the spectra indicate that exchange of aryl oxide ligands occurs at the same rate as exchange of nonequivalent xylyl methyl groups. Hence it appears that rotation about the *N*-xylyl bond is much slower than chelate inversion in these sterically congested complexes. These coordination properties of the enediamide ligand have been confirmed by a single-crystal X-ray analysis of complex **2b** (Figure 1).[9] It

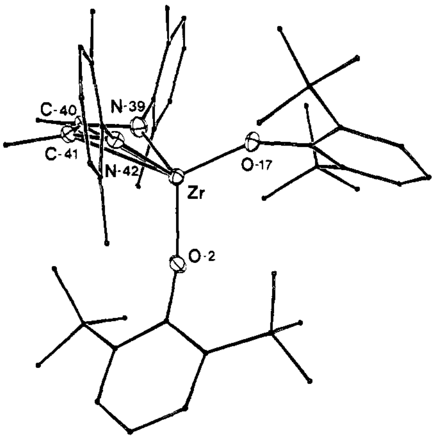
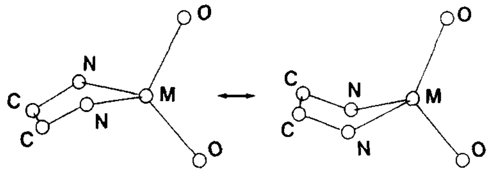


**Figure 1.** ORTEP view of $(Ar'O)_2Zr[C_8H_9NC(CH_3)C(CH_3)NC_8H_9]$ (**2b**) emphasizing the central coordination sphere. Important bond distances (Å) and angles (deg) are as follows: Zr–O(2) = 2.009 (4); Zr–O(17) = 1.950 (4); Zr–N(39) = 2.060 (6); Zr–N(42) = 2.061 (5); N(39)–C(40) = 1.420 (8); N(42)–C(41) = 1.439 (8); C(40)–C(41) = 1.366 (9); O(2)–Zr–O(17) = 114.1 (2); N(39)–Zr–N(42) = 84.1 (2); Zr–N(39)–C(40) = 102.0 (4); Zr–N(42)–C(41) = 99.4 (4); N(39)–C(40)–C(41) = 118.2 (6); N(42)–C(41)–C(40) = 120.0 (6).



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[2] (a) Moloy, K. G.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 7051. (b) Marks, T. J. *Science (Washington, D.C.)* **1982**, *217*, 989.

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[4] McMullen, A. K.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 1072.

[5] (a) $\mathbf{Zr(OAr')_2Me_2}$ was prepared by addition of 2,6-di-*tert*-butylphenol (Ar′OH; 2 equiv) to a solution of $ZrMe_4$ prepared from $ZrCl_4$ and MeMgI (4 equiv) in diethyl ether at −40 °C. Filtration, removal of solvent, and extraction with hexane gave the complex as a white, crystalline solid. (b) $\mathbf{Ti(OAr'')_2(CH_2Ph)_2}$ is obtained as a red, low melting solid on adding 2,6-di-isopropylphenol (Ar″OH; 2 equiv) to $Ti(CH_2Ph)_4$ in diethyl ether.

[6] **1a**: $^1H$ NMR (200 MHz, $C_6D_6$) δ 3.91 (s, $CH_2$Ph), 2.15 (s, $NC_6H_3Me_2$), 1.36 (d, $CHMe_2$), 3.82 (septet, $CHMe_2$); $^{13}C$ NMR (50.3 MHz, $C_6D_6$) δ 237.1 (xyNCCH₂Ph). **1b**: $^1H$ NMR (200 MHz, $C_6H_6$) δ 2.20 (s, $xyNCCH_3$), 1.70 (s, $NC_6H_3Me_2$), 1.52 (s, $CMe_3$); $^{13}C$ NMR (50.3 MHz, $C_6D_6$) δ 245.2 (xyNCMe).

[7] **2a**: $^1H$ NMR ($C_6D_5CD_3$, 90 MHz) + 70 °C, δ 4.21 (s, $CH_2$Ph), 2.05 (s, $NC_6H_3Me_2$), 1.15 (d, $CHMe_2$), 3.46 (septet, $CHMe_2$), −10 °C, δ 4.35, 3.60 (d, $CH_2$Ph), 2.21, 1.78 (s, $NC_6H_3Me_2$), 0.8–1.4 (overlapping doublets, $CHMe_2$), 3.50 br, $CHMe_2$). **2b**: $^1H$ NMR ($C_6D_5CD_3$, 90 MHz) + 45 °C, δ 1.75 (s, $CCH_3$), 2.18 (s, $NC_6H_3Me_2$), 1.35 (s, *t*-Bu), −20 °C, δ 1.70 (s, $CCH_3$), 2.15, 2.32 (s, $NC_6H_3Me_2$), 1.16, 1.34 (s, *t*-Bu).

[8] Kruger, C.; Muller, G.; Erker, G.; Dorf, V.; Engel, K. *Organometallics* **1985**, *4*, 215.

[9] Crystal data for $ZrC_{48}H_{66}N_2O_2$ (**2b**) at −161 °C: space group $P2_1/n$, $a$ = 17.653 (6) Å, $b$ = 14.820 (5) Å, $c$ = 16.510 (3), $\beta$ = 95.60 (5)°, $Z$ = 4, $d_{calcd}$ = 1.230 g cm⁻³. Of the 5594 unique reflections collected using Mo K α radiation between $6° \leq 2\theta \leq 45°$, the 3729 with $F > 3.00\sigma(F)$ were used in the full-matrix refinement. Final residuals are $R_F$ = 0.063 and $R_{wF}$ = 0.056.

can be seen that the two aryl oxides and enediamide chelate generate a pseudotetrahedral coordination about the zirconium atom. The lack of planarity of the 5-membered chelate ring is clearly evident although the distances from the metal to the carbon atoms of this ring are long, lying between 2.6 and 2.8 Å. It is interesting to note that the enediamide ligand is less distorted from planarity in the solid state than the analogous enamidolate[4] (folding angles of 37.8 (7)° and 50.0 (6)°, respectively) although the latter shows much more rapid chelate "inversion" in solution.

Preliminary kinetic measurements on this coupling process at zirconium, **1b** → **2b**, show the reaction to be a unimolecular process with activational parameters $\Delta H^{\ddagger} = 24.4 \pm 1.0$ kcal mol$^{-1}$ and $\Delta S^{\ddagger} = -16 \pm 5$ eu (105–145 °C temperature range). The moderately large and negative entropy of activation possibly reflects the necessity of the $\eta^2$-iminoacyl groups to both rotate into a coplanar geometry prior to coupling.

In contrast to this behavior, the monocyclometalated complex $Ti(OC_6H_3\text{-}t\text{-}BuCMe_2CH_2)(OAr')(CH_2SiMe_3)$[10] will rapidly insert 2 equiv of xyNC (as indicated both by mass spectrometry and microanalysis) to give high yields of a coupled product (**3**) immediately (Scheme I). The $^1H$ NMR spectrum of this compound is considerably more complex than that of the coupled products previously isolated. However, the spectrum is consistent with the molecular geometry shown (Scheme I) in which the titanium metal atom is surrounded by an aryl oxide group (OAr′) as well as an unusual *tris*-anionic, multidentate ligand coordinated to the metal through oxygen, nitrogen, and carbon atoms forming both a five- and eight-membered chelate ring. Preliminary X-ray diffraction data on complex **3** confirms this molecular structure in the solid state.[11] There are a number of possible pathways that can lead to this product following initial insertion into both of the metal–carbon bonds. One possibility is the isomerization of an intermediate, chelating enediamide by activation of the carbon–hydrogen bonds of the $CH_2SiMe_3$ substituent on the chelate ring,[12] while a second possibility involves an intramolecular trans coupling of the $\eta^2$-iminoacyls[13] followed by a metal-mediated hydrogen transfer from the $CH_2SiMe_3$ group to the nitrogen atom. The final product **3** can be described as containing an azametallocyclopentene ring with an amine substituent on the backbone.

**Acknowledgment.** We thank the National Science Foundation (Grant CHE-821906 to I.P.R.) for support of this research.

**Supplementary Material Available:** Listings of atomic coordinates and temperature factors (5 pages). Ordering information is given on any current masthead page.

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[10] Latesky, S. L.; McMullen, A. K.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.*, in press.

[11] Huffman, J. C., private communication.

[12] Isomerization of an azametallocyclopentene ring by a titanium metal atom mediated hydrogen shift between nitrogen and carbon has been reported; see: Cohen, S. A., Bercaw, J. E. *Organometallics* **1985**, *4*, 1006.

[13] The comparable stability and interconvertability of *cis*- and *trans*-butadiene ligands bound to $Cp_2Zr$ units has been well documented; see: Erker, G.; Wicker, J.; Engel, K.; Rosenfeldt, F.; Dietrich, W.; Kruger, C. *J. Am. Chem. Soc.* **1980**, *102*, 6344.

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# Synthesis and Crystal Structure of $(\mu\text{-}H)Os_3(CO)_9(\eta^1\text{-}C(OMe)_2)(\mu_3\text{-}CPh)$, a Mixed Carbene–Carbyne Cluster Complex

**John R. Shapley* and Wen-Yann Yeh**

*Department of Chemistry, University of Illinois*
*Urbana, Illinois 61801*

**Melvyn Rowen Churchill* and Yong-Ji Li**

*Department of Chemistry*
*University at Buffalo, State University of New York*
*Buffalo, New York 14214*

*Received May 22, 1985*

*Summary:* The complex $(\mu\text{-}H)Os_3(CO)_9(\eta^1\text{-}C(OMe)_2)(\mu_3\text{-}CPh)$ (**1**) is formed by sequential treatment of $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}COMe)$ with PhLi and $MeOSO_2CF_3$ at 0 °C. The osmium triangle is semi-triply-bridged by a benzylidyne ligand (Os(2)–C(3) = 2.074 (14) Å, Os(3)–C(3) = 2.040 (15) Å, and Os(1)···C(3) = 2.286 (12) Å), and a dimethoxycarbene ligand takes up an equatorial site on Os(1). Further treatment of **1** with $MeOSO_2CF_3$ yields $(\mu\text{-}H)Os_3(CO)_{10}(\mu_3\text{-}CPh)$ and $Os_3(CO)_9(\mu_3\text{-}CPh)(\mu_3\text{-}COMe)$.

The COMe → CH transformation shown in eq 1 proceeds through the isolable intermediate $[(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}CHOMe)^-]$, demonstrating nucleophilic attack at the carbyne center.[1] Recently, we showed that an analogous set of nucleophilic/electrophilic treatments can effect the COMe → CPh transformation shown in eq 2.[2]

$$(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}COMe) \xrightarrow[2.\ H^+]{1.\ H^-} (\mu\text{-}H)Os_3(CO)_{10}(\mu_3\text{-}CH) \quad (1)$$

$$(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}COMe) \xrightarrow[2.\ Me^+]{1.\ Ph^-} (\mu\text{-}H)Os_3(CO)_{10}(\mu_3\text{-}CPh) \quad (2)$$

However, by modifying the reaction conditions in (2), we have now isolated and characterized an intermediate, the structure of which is not only unusual but indicates an entirely different pathway for (2) compared with (1).

Slow addition of PhLi (1.8 M, benzene/ether, 2.5 equiv) to a solution of $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}COMe)$ (330 mg, 0.37 mmol) in freshly distilled diethyl ether (150 mL) at 0 °C under nitrogen produced an orange-red, cloudy solution. $MeOSO_2CF_3$ (4 equiv) was then added via a syringe. The solution was concentrated to ca. 10 mL under vacuum, then placed under nitrogen, and stirred for 30 min at 0 °C, at which point the solution became clear. The volatile materials were removed under vacuum, and the orange residue was purified by preparative TLC (silica gel), eluting with *n*-pentane/dichloromethane (4:1, v/v). Crystallization

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[1] Shapley, J. R.; Cree-Uchiyama, M. E.; St. George, G. M.; Churchill, M. R.; Bueno, C. *J. Am. Chem. Soc.* **1983**, *105*, 140.

[2] Yeh, W.-Y.; Shapley, J. R.; Li, Y.-J.; Churchill, M. R. *Organometallics* **1985**, *4*, 767.

[3] **1**: mp 121–123 °C; mass spectrum (field desorption), *m/z* 992 ($M^+$, $^{192}Os$); IR ($C_6H_{12}$) $\nu$ (CO) 2091 (m), 2081 (m), 2053 (s), 2029 (s), 2000 (s), 1989 (m), 1980 (m), 1966 (sh), 1955 (sh) cm$^{-1}$; $^1H$ NMR ($CD_2Cl_2$, 17 °C, mixture of two isomers, A and B, A:B = 0.7:1) $\delta$ 7.57–7.13 (m, $C_6H_5$), 4.00 (s, $CH_3$(B)), 3.88 (s, $CH_3$(A)), −16.66 (s, $\mu$-H(A)), −17.40 (s, $\mu$-H(B)); $^{13}C$ NMR (THF-$d_8$ + THF (1:1), 17 °C) $\delta$ 252.0 ($\equiv$C(B)), 238.4 ($\equiv$C(A)), 222.6 (=C(A)), 214.8 (=C(B)), 185–170 (CO). Anal. Calcd for $Os_3C_{19}H_{12}O_{11}$: C, 23.12; H, 1.22; Os, 57.82. Found: C, 23.32; H, 1.23; Os, 57.6.

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