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Full Paper

Nitrosyl Mo Complexes

Ullmann-Type and Related Redox Reactions of Nitrosyl Molybdenum Complexes Bearing a Large-Bite-Angle Diphosphine

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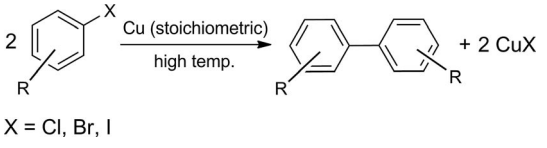
Abstract: The reactions of ArX (X = Cl and Br) with $[Mo(NO)(P\cap P)(NCMe)_3][BAr^F{}_4]$ P∩P = 2,2′-bis(diphenylphosphanyl)diphenyl ether (DPEphos), $BAr^F{}_4$ = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate at 120 °C resulted in the formation of biphenyl (through C_{Ar}–C_{Ar} reductive homocoupling) and the dinuclear halide salts $[Mo_2(NO)_2(P\cap P)_2(NCMe)_2(\mu\text{-}X)_2][BAr^F{}_4]_2$ (X = Cl, **1**; Br, **2**). Complexes **1** and **2** potentially show *cisoid* (**1c** and **2c**) and *transoid* (**1t** and **2t**) regioisomerism with respect to the position of the NO ligand. The crystal-structure determinations of **1** and **2** revealed the presence of the *transoid* isomers **1t** and **2t** and M^I–M^I bonding in both cases. A proposed mechanism for the formation of **1t** and **2t** involves reductive C_{Ar}–C_{Ar} coupling to form biphenyl from two Ph–Mo^{II} centers. In addition, the complexes $Mo(NO)(P\cap P)(CO)_2Cl$ (**3**) and [Mo(NO)(*mer*-κ³-*P,P,O*-DPEphos)Cl(PR_3)] (R = Me, **4**; Ph, **5**) were obtained through the reductions of $[Mo_2(NO)_2(P\cap P)_2Cl_4(\mu\text{-}Cl)_2]$.

Introduction

Organometallic complexes of group VI metals show an extensive redox chemistry covering the M^{II}, M^I, and M^0 oxidation states; however, quite strong reducing agents are required to go from M^{II} to M^0 species. Mild reducing agents are expected to stop the reduction process at the stage of the M^I species, as are mild oxidizing agents when coming from M^0 complexes. In this study, it was found that aryl halides behave as mild oxidizing agents towards $[Mo(NO)(P\cap P)(NCMe)_3]^+$ cations [P∩P = 2,2′-bis(diphenylphosphanyl)diphenyl ether (DPEphos)] and provoke C_{Ar}–C_{Ar} homocoupling to form the biaryl structural motif, which is the core of a wide range of functional molecules, natural products, commercial dyes, and the backbones of various ligands used for asymmetric catalysis.[1] The first C_{Ar}–C_{Ar} bond formation was reported in 1901 by Ullmann and was achieved through the reductive homocoupling of aryl halides by employing stoichiometric amounts of finely divided copper at high temperature (above 200 °C) to form biaryls and copper halides (Scheme 1).[2] Since then, the application of the Ullmann reaction has become of paramount importance and has revealed quite general applicability in the synthesis of many symmetric and unsymmetric biaryls and polyaryls.[3]

Nevertheless, the harsh reaction conditions, stoichiometric amount of the Cu reagent, and longer reaction times typically required for Ullmann coupling have motivated the search for milder variations,[4,5] and Pd catalyzed C–C cross-coupling reactions have become a viable synthetic route to such biaryl cores.[6–9] However, Pd systems suffer from toxicity and cost issues, which prompted researchers to refocus on the development of efficient Cu-mediated Ullmann-type reactions with various ligands as additives.[10,11] Lately, several groups have demonstrated Ullmann-type coupling reactions,[12–14] including the intermolecular chiral synthesis of biaryls.[15]



Scheme 1. Cu-mediated Ullmann coupling of aryl halide.

In conjunction with Cu-mediated Ullmann-type coupling reactions, a modern prerequisite of metal-promoted organic chemistry is the exploration of the cheap, low toxicity, and environmentally benign middle transition elements Fe, Mo, and W as surrogates for precious metal catalysts in homogeneous catalysis.[16] Lately, our group has developed several Mo- and W-based highly efficient hydrogenation catalysts, which showed that complexes of middle transition elements can also take over functions that are normally attributed solely to platinum-group metal centers.[17] In this regard, the exploitation of a suitable group VI complex in Ullmann-type C_{Ar}–C_{Ar} coupling reactions would also be highly desirable. Furthermore, from a mechanistic point of view, the observation of C_{Ar}–C_{Ar} bond formations through dinuclear reductive elimination are quite rare.[18] In 2001, Anderson and co-workers demonstrated the reductive elimination of 1,2-diphenylethane from the "A-frame" dinuclear $[Pd_2(CH_2Ph)_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]X$ [X = Cl^-, PF_6^-; dppm = 1,1-bis(diphenylphosphanyl)methane] system.[19] The elimination of diphenylethane was envisaged to occur through mononuclear reductive elimination, in which the eliminated organic groups must first become bonded to the same palladium center. Bera and co-workers demonstrated Suzuki cross-coupling reactions

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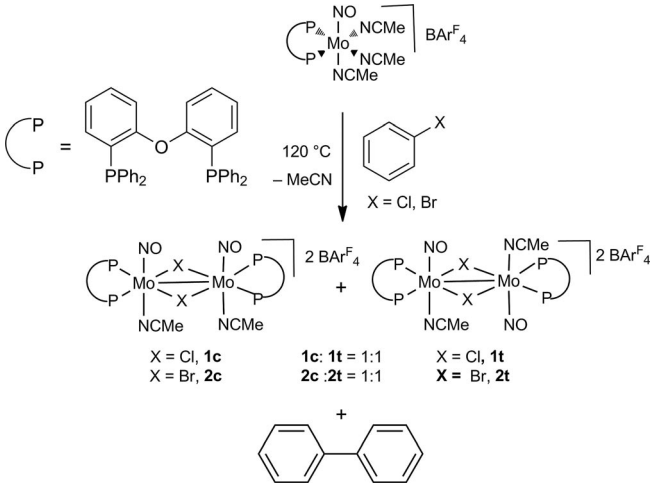
of aryl halides catalyzed by a dipalladium(I) system $[Pd_2L_2][BF_4]_2$ [L = [(5,7-dimethyl-1,8-naphthyridin-2-yl)-amino]carbonylferrocene].[20] One of the proposed catalytic steps was the dinuclear reductive elimination of C–C bonds from two Pd^{II} centers to give coupled Pd^{I} centers. However, solid mechanistic evidence for the proposed catalytic step could not be provided. Johnson and co-worker synthesized tetraphenylene from biphenylene mediated by a dinuclear Ni^{I}–Ni^{I} species, and the C–C bond formation occurred in a dinuclear fashion, as supported by a deuterium labeling study and crossover experiments,[21] and Jones and co-workers demonstrated a mononuclear mechanism for the catalytic conversion of biphenylene to tetraphenylene through reductive C–C elimination by applying Pt and Pd metal centers.[22]

In a previous publication,[23] we reported the preparation of $[Mo(NO)(P\cap P)(NCMe)_3][BAr^F{}_4]$ $BAr^F{}_4$ = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate, which could be employed as an effective catalyst for hydrosilylation reactions of various aldehydes, ketones, and imines. Herein, we demonstrate the unique use of this complex for an Ullmann-type two-centered reductive homocoupling process of aryl halides (X = Cl and Br) to form biphenyl and dinuclear Mo^{I}–Mo^{I} bonded species.

Results and Discussion

Preparation of Dinuclear $[Mo_2(NO)_2(P\cap P)_2(NCMe)_2(\mu\text{-}X)_2][BAr^F{}_4]_2$ Complexes

The treatment of $[Mo(NO)(P\cap P)(NCMe)_3][BAr^F{}_4]$ with chlorobenzene at 120 °C for 30 min resulted in the formation of an isomeric mixture of the dinuclear $[Mo_2(NO)_2(P\cap P)_2(NCMe)_2(\mu\text{-}Cl)_2][BAr^F{}_4]_2$ (**1c** and **1t**) complexes in 92 % yield (Scheme 2).



Scheme 2. Reaction scheme for the formation of biphenyl and dinuclear molybdenum complexes of type **1** and **2**.

The $^{31}P^{1}H$ NMR spectrum of **1** showed four doublet signals at δ = 37.8 (**1t**), 34.2 (**1c**), 29.9 (**1c**) and 27.1 ppm (**1t**); this supports the formation of the dinuclear isomers **1c** and **1t** (1:1 ratio, as revealed by the $^{31}P^{1}H$ NMR spectra), which differ in the relative position of the nitrosyl ligands in the dinuclear arrangements, namely, *cisoid* (**1c**) and *transoid* (**1t**). The four doublet signals in the $^{31}P^{1}H$ NMR spectrum could be grouped into pairs on the basis of their coupling constants [**1t**: δ = 37.8 and 27.1 ppm ($^{2}J_{P,P}$ = 108.7 Hz); **1c**: δ = 34.2 and 29.9 ppm ($^{2}J_{P,P}$ = 109.3 Hz)], which indicated the inequivalence of the two phosphorus atoms of one bidentate ligand in both isomers. This is presumably because of the "twisted" conformation of the rigid large-bite-angle DPEphos ligand, which also induces asymmetry in the chlorido bridges. Crystallization from a chlorobenzene/pentane mixture at room temperature afforded single crystals of **1t** suitable for an X-ray diffraction study, which revealed that the cationic dinuclear unit of **1t** consists of two [Mo(NO)(P∩P)(NCMe)] units with the NO ligands of the two complex units in a *transoid* arrangement and held together by the two μ-Cl bridges (Figure 1). The twisted conformation of the DPEphos ligand forces one phenyl ring of the backbone to be located more axially *cisoid* to the acetonitrile ligand, and the other phenyl ligand is arranged more equatorially between the MeCN and NO ligands to generate helical twists of the rigid DPEphos backbones with opposite helicities at both Mo centers. The bridging chlorido ligands support the 18e⁻ configuration of the M–M fragment[24] and the overall diamagnetism. Complex **1t** crystallizes in the triclinic $P\bar{1}$ space group. The asymmetric unit of the crystals contains the cationic part of **1t**, the $[BAr^F{}_4]^-$ counteranions, and pentane and chlorobenzene solvate molecules. The average Mo–P bond length is 2.6188 Å, and the bridging Mo–Cl distances are 2.409(17) and 2.4106(16) Å. The Mo1–Mo1 bond length of 3.0162(10) Å lies in the range expected for bridge-supported Mo–Mo contacts.[25] The formation of the *cisoid* isomer **1c** with the nitrosyl ligands of the dinuclear species on the same side was also evident from analysis of the $^{31}P^{1}H$ COSY and 1D NOE spectra. In the ^{1}H NMR spectrum, the methyl protons of the attached CH_3CN ligand appeared at δ = 1.9 and 1.8 ppm in a 1:1 intensity ratio (assigned to **1t** and **1c**, respectively). The composition of the isomeric mixture of **1c** and **1t** was further confirmed by elemental

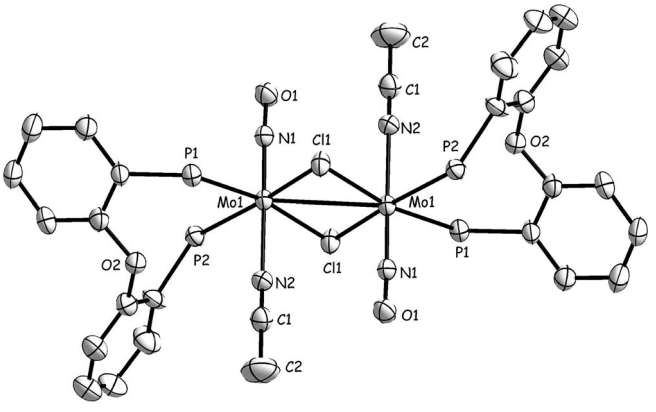


Figure 1. Molecular structure of the cationic part of **1t**. Thermal ellipsoids are drawn at the 50 % probability level. All hydrogen atoms, phenyl rings, pentane and C_6H_5Cl solvate molecules, and $[BAr^F{}_4]^-$ counteranions are omitted for clarity. Selected bond lengths [Å] and angles [°]: Mo1–N1 1.779(6), Mo1–N2 2.188(6), Mo1–Cl1 2.4189(17), Mo1–Cl1i 2.4106(16), Mo1–P1 2.6270(17), Mo1–P2 2.6106(17), Mo1–Mo1 3.0162(10), N1–O1 1.178(7), N1–Mo1–N2 177.43(2), P1–Mo1–P2 97.92(5), P1–Mo1–Cl1 167.85(6), Cl1–Mo1–Cli 102.70(5), Cl1–Mo1–Mo1i 51.23(4), Cl1–Mo1i–Mo1 51.47(4). Symmetry operation, i: –*x*, 1 – *y*, 1 – *z*.

analysis. The formation of **1t** or **1c** was mechanistically explained on the basis of the oxidative addition of chlorobenzene to the cationic complex $[Mo(NO)(P\cap P)(NCMe)_3][BAr^F_4]$ through the replacement of one MeCN ligand. Subsequently, the dinuclear adduct with chlorido bridges is envisaged to undergo dinuclear elimination of biphenyl through C_{Ar}–C_{Ar} coupling to generate the Mo^I–Mo^I bonded isomers **1c** and **1t**. Thus, the biphenyl formation is anticipated to result from dinuclear reductive coupling and is supported by the conspicuous mononuclear fragment at *m/z* = 154 in the GC–MS spectra. However, another more complex reaction path with mononuclear C_{Ar}–C_{Ar} bond formation can also be envisaged, as shown in Scheme 3.

To put the production of biphenyl and the formation of the dinuclear species of type **1** on more general grounds, we also probed the reaction of $[Mo(NO)(P\cap P)(NCMe)_3][BAr^F_4]$ with bromobenzene at 120 °C in tetrahydrofuran (THF). This reaction was monitored by $^{31}P^1H$ NMR spectroscopy, which revealed the appearance of four doublet signals at δ = 37.4 and 26.1 ppm ($^2J_{P,P}$ = 107.1 Hz) and δ = 33.8 and 29.6 ppm ($^2J_{P,P}$ = 108.4 Hz). This is consistent with the formation of an isomeric mixture of the dinuclear species $[Mo_2(NO)_2(P\cap P)_2(NCMe)_2(\mu\text{-}Br)_2][BAr^F_4]_2$ (**2t** and **2c**) if it is assumed that the phosphorus atoms at each molybdenum center of **2t** and **2c** are inequivalent (Scheme 2). The reaction was complete in 1 h, and the isomeric product mixture was obtained in 82 % yield.

In the ^1H NMR spectrum, the methyl protons of the acetonitrile ligand appeared at δ = 2.3 and 2.4 ppm in an approximate 1:1 intensity ratio for **2t** and **2c**, respectively. The slow diffusion of pentane into a concentrated C_6H_5Cl solution at room temperature produced deep red crystals of **2t**, which were suitable for an X-ray diffraction study. Complex **2t** is isostructural to **1t** and crystallizes in the triclinic space group $P\bar{1}$. The molecular structure of $[Mo^I(NO)(P\cap P)(NCMe)(\mu\text{-}Br)]_2^{2+}$ was similar to that of **1t**; two [Mo(NO)(P∩P)(NCMe)] cationic units are held together by two μ-Br bridges with bridging Mo–Br bond lengths of 2.5043(8) and 2.5211(8) Å, and the mononuclear units have a *transoid* arrangement (Figure 2). The unit cell additionally contains two $BAr^F_4{}^-$ anions and three chlorobenzene solvate molecules. The Mo–P distances are in the expected range, and the P–Mo–P angles are 96.99(4)°. The Mo1–Mo1 bond length of 3.0614(7) Å is in the range expected for a bridge-supported Mo–Mo contact and is very close to that of **1t**.[25] The crystallographic data of **1t** and **2t** are given in Table 1. The GC–MS analysis of the pentane-extracted part of the **2t** and **2c** reaction mixture revealed the presence of biphenyl as a product from the clear mononuclear fragment at *m/z* = 154. The formation of the dinuclear species of types **1** and **2** could be envisaged according to Scheme 3. First, Ar–X (X = Cl, Br) exchanges with a labile MeCN ligand of $[Mo(NO)(P\cap P)(NCMe)_3]^+$ and subsequent oxidative addition leads to Mo^{II} halophenyl species of type **I-1**, which could then dimerize to the dinuclear intermediates **I-2**. Supported by the presence of the large-bite-angle diphosphine, the reductive elimination of diphenyl could occur from **I-2** or **I-3** to generate the metal–metal bonds of **1** and **2**. A mononuclear pathway invoked by Osakada et al.[26] cannot be excluded but seems less probable. In this pathway, two molecules of the oxidatively added **I-1** may undergo "symmetrization" through halide and aryl exchange to form the two Mo^{II} species of type **I-3** and **I-3′**; after reductive elimination from **I-3** and comproportiona-

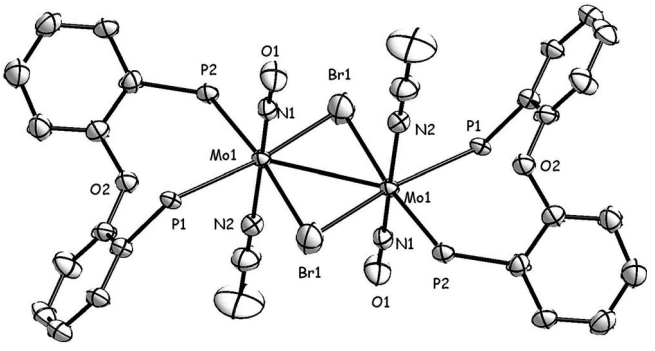
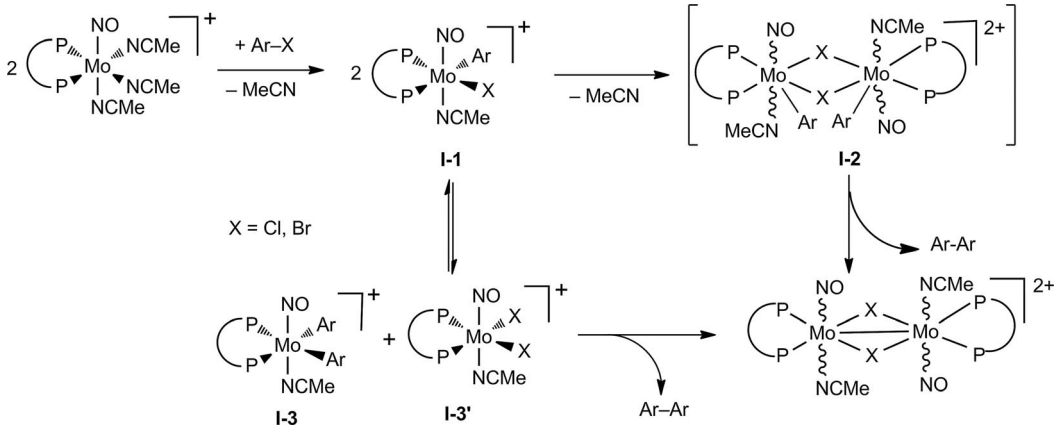


Figure 2. Molecular structure of the cationic part of **2t**. Thermal ellipsoids are drawn at the 50 % probability level. All hydrogen atoms, phenyl rings, C_6H_5Cl solvate molecules, and $[BAr^F_4]^-$ counteranions are omitted for clarity. Selected bond lengths [Å] and angles [°]: Mo1–N1 1.773(4), Mo1–N2 2.201(4), Mo1–Br1 2.5043(8), Mo1–Br1i 2.5211(8), Mo1–P1 2.6212(12), Mo1–P2 2.6119(12), Mo1–Mo1 3.0614(7), N1–O1 1.185(6), N1–Mo1–N2 176.53(18), P1–Mo1–P2 96.99(4), P1–Mo1–Br1 172.79(3), Br1–Mo1–Bri 104.94(2), Br1–Mo1–Mo1i 52.720(19), Br1–Mo1i–Mo1 52.220(19). Symmetry operation, i: –*x*, 1 – *y*, 1 – *z*.



Scheme 3. Alternative reaction courses for the formation of $[Mo^I(NO)(P\cap P)(NCMe)(\mu\text{-}Br)]_2^{2+}$ and biphenyl involving the oxidative addition to **I-1** followed by dinuclear reductive elimination of biphenyl or scrambling to form **I-3** and **I-3′** after the oxidative addition to **I-1**.

tion with **I-3'**, the isomeric dinuclear complexes are formed followed by concomitant reductive elimination of biphenyl from **I-3**. The resulting $[Mo^0(NO)(P\cap P)(NCMe)]^+$ species compropportionates with **I-3'** to give the dinuclear complexes of type **1** or **2**.

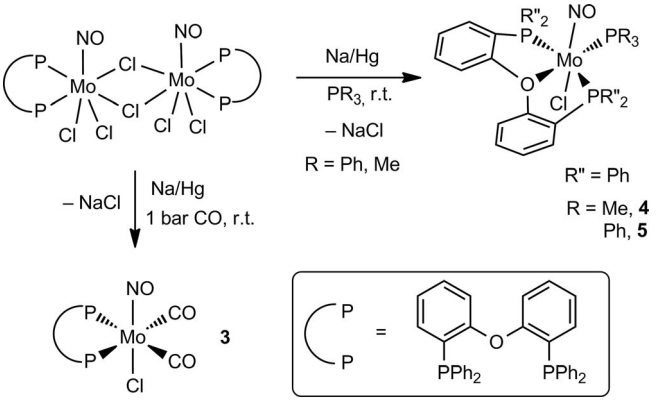
Table 1. Crystallographic data for **1t** and **2t**.[a]

	1t	**2t**
Empirical formula	$C_{76}H_{62}Cl_2Mo_2N_4O_4P_4$·2($C_{32}H_{12}BF_{24}$)·$C_5H_{12}$·$C_6H_5Cl$	$C_{76}H_{62}Br_2Mo_2N_4O_4P_4$·2($C_{32}H_{12}BF_{24}$)·3($C_6H_5Cl$)
Formula weight /g mol^{-1}	3393.10	3634.98
Temperature /K	183(2)	183(1)
Wavelength /Å	0.71073	0.71073
Crystal system, space group	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$
a /Å	16.0776(9)	13.6800(2)
b /Å	17.0716(13)	17.6953(3)
c /Å	18.0135(14)	19.7075(4)
α /°	105.257(7)	113.853(2)
β /°	115.011(7)	98.357(2)
γ /°	98.938(5)	98.951(2)
Volume /Å^3	4116.7(6)	4193.93(13)
Z, density (calcd.) /Mg m^{-3}	1, 1.369	1, 1.439
Absorption coefficient /mm^{-1}	0.344	0.817
F(000)	1706	1816
Crystal size /mm	0.38 × 0.28 × 0.06	0.50 × 0.24 × 0.11
θ range /°	2.82 to 25.03	2.08 to 27.48
Reflections collected	43069	68102
Reflections unique	14519 (R_{int} = 0.0745)	19225 (R_{int} = 0.0372)
Completeness to *θ* /%	99.8	100.0
Absorption correction	analytical	analytical
Max./min. transmission	0.978 and 0.914	0.916 and 0.720
Data/restraints/parameters	10291/238/1064	15522/325/1242
Goodness-of-fit on F^2	1.179	1.053
Final R_1 and wR_2 indices [$I > 2\sigma(I)$]	0.1156, 0.2968	0.0884, 0.2602
R_1 and wR_2 indices (all data)	0.1467, 0.3276	0.1061, 0.2807
Largest diff. peak and hole /e Å^{-3}	6.031 and –1.128	2.392 and –3.954

[a] The unweighted *R* factor is $R_1 = \Sigma(F_o - F_c)/\Sigma F_o$ and the weighted *R* factor is $wR_2 = \Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^{21/2}$.

Preparation of Low-Valent DPEphos Mo^0 Complexes

Although the soft oxidation of the $[Mo(NO)(P\cap P)(NCMe)_3]^+$ complexes by aryl halides led to the dinuclear species of type **1** or **2**, stronger reducing agents such as 1 % Na/Hg reduce the dinuclear $[Mo_2(NO)_2(P\cap P)_2Cl_4(\mu\text{-}Cl)_2]$ complex[23] to various low-valent Mo^0 complexes in the presence of strongly coordinating π-accepting or σ-donating ligands such as CO and PR_3 (R = Me and Ph). The reaction of $[Mo_2(NO)_2(P\cap P)_2Cl_4(\mu\text{-}Cl)_2]$ with excess 1 % Na/Hg (5 equiv.) in the presence of 1 bar of carbon monoxide at room temperature produced $Mo(NO)(P\cap P)(CO)_2Cl$ (**3**, Scheme 4). However, the yield was quite low (20 %) owing to the formation of other unidentified products. Nevertheless, **3** could be prepared in excellent yield (76 %) by a modified synthetic procedure from the $Mo(NO)(CO)_4(ClAlCl_3)$ precursor[27] and the DPEphos ligand at 70 °C in THF. The $^{31}P^1H$ NMR spectrum of the resulting mixture displayed only a sharp singlet resonance at δ = 16.6 ppm owing to the presence of **3** and supported the equivalence of the P atoms of the DPEphos ligands and the apparent absence of stereoisomers in solution. The IR spectrum showed strong absorptions at $\tilde{\nu}$ = 2028 and 1957 cm^{-1} assigned to the ν_{CO} stretching vibration in addition to the ν_{NO} stretching frequency at $\tilde{\nu}$ = 1630 cm^{-1}.



Scheme 4. Synthetic access to various low-valent Mo^0 complexes bearing the large-bite-angle DPEphos ligand.

The ^1H NMR spectrum of **3** in CD_2Cl_2 at room temperature revealed several signals in the expected aromatic region for the attached DPEphos ligand. Single crystals suitable for X-ray diffraction studies were obtained from a toluene/pentane mixture at room temperature. The X-ray structure analysis showed that the two carbonyl ligands and the two phosphorus atoms of the DPEphos ligand occupy the equatorial plane (Figure 3). The *trans* NO/Cl axis was disordered with a site-occupancy ratio of 0.776:0.224(1). The composition of the compound was further confirmed by elemental analysis.

The monodentate phosphine complexes $Mo(NO)(P\text{–}O\text{–}P)(PR_3)Cl$ (R = Me, **4**; Ph, **5**) were prepared by the reactions of $[Mo_2(NO)_2(P\cap P)_2Cl_4(\mu\text{-}Cl)_2]$ with 1 equiv. of the PR_3 derivative (R = Me and Ph) in the presence of excess 1 % Na/Hg (5 equiv.) in THF at room temperature and isolated as red (**4**, 50 %) and orange (**5**, 55 %) solids in moderate yields. It should be mentioned at this point that the employment of 2 equiv. of these monophosphines did not allow the further incorporation of phosphine ligands, apparently owing to the bulkiness of the DPEphos ligand. The $^{31}P^1H$ NMR spectrum of **4** displayed a doublet of doublet signal for the coordinated P–O–P ligand at δ = 45 ppm ($^2J_{P,P}$ = 12 Hz) along with a triplet resonance at lower field (δ = 26 ppm, $^2J_{P,P}$ = 12 Hz) for the PMe_3 ligand. On the other hand, **5** exhibited a triplet signal at δ = 74 ppm ($^2J_{P,P}$ = 12 Hz) for the attached triphenylphosphine ligand, and the phosphorus resonance of the DPEphos ligand was transformed into two doublet of doublet signals (ABX spin system) with a strong *trans* $^2J_{P,P}$ coupling of 165 Hz at δ = 43 and 37 ppm ($^2J_{P,P}$ = 12 Hz). The inequivalence of the two phosphorus atoms within the η^3 chelate arises from a rigid conformation of the complexed ligand, as is typical for large-bite-angle diphosphines, for which the four P-bound phenyl rings adopt pseudo-axial and pseudoequatorial positions that result in different conformations at each P atom with the consequence that inver-

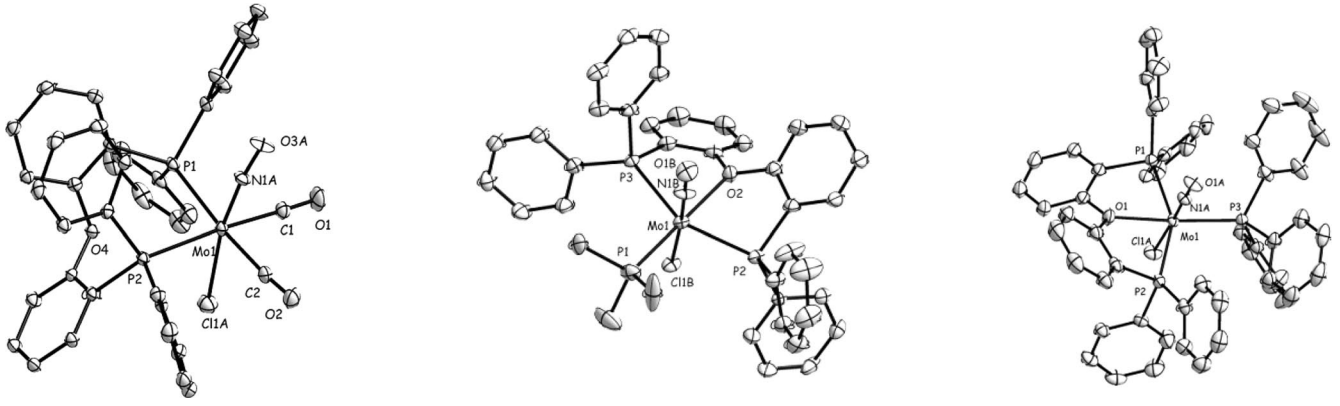


Figure 3. Molecular structures of **3** (left), **4** (middle), and **5** (right). Thermal ellipsoids are drawn at the 30 % (for **3** and **4**) and 50 % (for **5**) probability levels. All hydrogen atoms and solvent molecules are omitted for clarity. The *trans* NO/Cl ligands are disordered with a site-occupancy ratio of 0.776:0.224. Selected bond lengths [Å] and angles [°]: **3**: Mo1–N1A 1.815(2), Mo1–C1 2.0172(16), Mo1–C2 2.0282(18), Mo1–Cl1A 2.4554(8), Mo1–P1 2.6011(4), Mo1–P2 2.6209(4), N1A–O3A 1.283(2), C1–O1 C2–O2, N1A–Mo1–Cl1A 169.91(7), N1A–Mo1–C2 85.34(8), P1–Mo1–P2 96.039(13), P1–Mo1–C2 175.17(5), P1–Mo1–C1 85.96(5); **4**: Mo1–N1B 1.771(14), Mo1–O2 2.266(2), Mo1–P1 2.3740(11), Mo1–P2 2.4432(10), Mo1–P3 2.4599(9), N1B–O1B 1.27(3), N1B–Mo1–Cl1B 176.4(4), P1–Mo1–N1B 84.4(4), P2–Mo1–P3 152.23(3), P1–Mo1–P3 104.62(4); **5**: Mo1–N1A 1.745(4), Mo1–O1 2.2914(10), Mo1–P1 2.4681(3), Mo1–P2 2.4840(3), Mo1–P3 2.4225(4), N1A–O1A 1.198(4), N1A–Mo1–Cl1A 176.89(16), P1–Mo1–N1A 95.41(15), P1–Mo1–P3 101.565(11), P1–Mo1–P2 151.326(13).

Table 2. Crystallographic data for **3**, **4**, and **5**.

	3	**4**	**5**
Empirical formula	$C_{38}H_{28}ClMoNO_4P_2 \cdot C_7H_8$	$2(C_{39}H_{37}ClMoNO_2P_3) \cdot C_4H_{10}O$	$C_{54}H_{43}ClMoNO_2P_3$
Formula weight /g mol^{-1}	848.08	1626.11	962.19
Temperature /K	183(2)	183(2)	183(2)
Wavelength /Å	0.71073	0.71073	0.71073
Crystal system, space group	monoclinic, $P2_1/c$	monoclinic, $P2_1/n$	monoclinic, $P2_1/n$
a /Å	11.5883(1)	10.2639(1)	19.3956(3)
b /Å	13.8586(1)	21.2569(3)	12.6738(2)
c /Å	24.9475(2)	18.3320(3)	20.4746(3)
α /°	90	90	90
β /°	101.155(1)	105.192(2)	114.639(2)
γ /°	90	90	90
Volume /Å^3	3930.82(5)	3859.88(10)	4574.74(14)
Z, density (calcd.) /Mg m^{-3}	4, 1.433	2, 1.399	4, 1.397
Absorption coefficient /mm^{-1}	0.528	0.571	0.493
F(000)	1736	1676	1976
Crystal size /mm	0.28 × 0.12 × 0.12	0.26 × 0.16 × 0.07	0.44 × 0.34 × 0.20
θ range /°	2.58 to 30.51	2.49 to 26.37	2.57 to 30.51
Reflections collected	67377	47560	96389
Reflections unique	12004 (R_{int} = 0.0321)	7882 (R_{int} = 0.0490)	13957 (R_{int} = 0.0307)
Completeness to *θ* /%	99.9	99.9	99.9
Absorption correction	analytical	analytical	analytical
Max./min. transmission	0.944 and 0.891	0.964 and 0.899	0.935 and 0.870
Data/restraints/parameters	9437/3/498	5943/166/547	11579/4/569
Goodness-of-fit on F^2	1.081	1.052	1.080
Final R_1 and wR_2 indices [$I > 2\sigma(I)$]	0.0323, 0.0809	0.0472, 0.1100	0.0270, 0.0714
R_1 and wR_2 (all data)	0.0450, 0.0834	0.0696, 0.1160	0.0361, 0.0733
Largest diff. peak and hole /e Å^{-3}	0.602 and –0.688	1.528 and –0.725	0.393 and –0.610

sions are not permitted. The molecular structures of **4** and **5** were determined by X-ray diffraction studies (Table 2) and are displayed in Figure 3 with selected bond lengths and angles. In both structures, the chelating phosphine ligand is tridentate through the P,O,P atoms in a meridional arrangement with *trans* P–Mo–P angles of 152.23(3)° for **4** and 151.326(13)° for **5**. The coordination of the oxygen atom is presumably preferred to allow the complexes to achieve 18-electron configurations[28] and is in accord with observations for related (DPEphos)Ru complexes. The Mo–$P_{chelate}$ bond lengths (2.44–2.48 Å) are slightly longer than the Mo–PR_3 bond lengths (ca. 2.37–2.42 Å), and the Mo–O bond lengths lie within the range 2.27–2.29 Å. Furthermore, **4** and **5** could be characterized fully by ^{1}H NMR spectroscopy, and their compositions were confirmed by elemental analysis.

Conclusions

We have discovered the mild oxidation of [Mo^0(NO)-(P∩P)(NCMe)$_3$][BAr^F_4] with aryl halides (ArX; X = Cl, Br) to form biphenyl and the dinuclear species [Mo^I_2 (NO)$_2$(P∩P)$_2$-

$(NCMe)_2(\mu\text{-}X)_2][BAr^F{}_4]_2$ (X = Cl, **1c** and **1t**; Br, **2c** and **2t**) through an Ullmann-type dinuclear homocoupling process. The dinuclear complexes **1c**/**1t** and **2c**/**2t** were characterized spectroscopically and by X-ray diffraction studies. We have also described the synthetic access to several DPEphos-containing low-valent complexes, namely, $Mo^0(NO)(P\cap P)(CO)_2Cl$ (**3**) and $Mo^0(NO)(P\text{–}O\text{–}P)(PR_3)Cl$ (R = Me, **4**; Ph, **5**), through the reductions of the dinuclear Mo^{II} compounds. This work, particularly the Mo-complex-mediated homocoupling process to form biphenyl, render the idea that Mo and W catalysts can be developed for catalytic C_{Ar}–C_{Ar} bond formations through further ligand tuning efforts and the involvement of a suitable redox couple.

Experimental Section

General Considerations: All manipulations were performed under an atmosphere of nitrogen by standard Schlenk techniques or in a glovebox. All reagent-grade solvents were dried according to standard laboratory procedures with CaH_2 (C_6D_5Cl and CD_2Cl_2) and distilled through freeze–pump–thaw cycles before use. $[Mo(NO)(P\cap P)(NCMe)_3][BAr^F{}_4]$, $[Mo_2(NO)_2(P\cap P)_2Cl_4(\mu\text{-}Cl)_2]$, and $Mo(NO)(CO)_4(ClAlCl_3)$ were prepared according to literature procedures.[23,27] All other chemicals were purchased from commercial sources and used without further purifications. The NMR spectra were recorded with Varian Mercury 200 (200.1 MHz for ^1H, 81.0 MHz for ^{31}P), Varian Gemini-300 (^1H at 300.1 MHz, ^{13}C at 75.4 MHz), Bruker-DRX 500 (500.2 MHz for ^1H, 202.5 MHz for ^{31}P, 125.8 MHz for ^{13}C), and Bruker-DRX 400 spectrometers (400.1 MHz for 1 H, 162.0 MHz for ^{31}P, 100.6 MHz for ^{13}C). The ^1H and $^{13}C\{^1H\}$ chemical shifts are expressed in ppm relative to tetramethylsilane (TMS), and the $^{31}P\{^1H\}$ chemical shifts are relative to 85 % H_3PO_4 as an external standard. The signal patterns are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. The IR spectra were obtained by attenuated total reflectance (ATR) or KBr methods with a Bio-rad FTS-45 instrument. The elemental analyses were performed at the Anorganisch-Chemisches Institut of the University of Zürich. The GC–MS spectra were recorded with a Varian Saturn 2000 spectrometer equipped with Varian 450-GC chromatograph Phenomenex ZB-5 ms (30 m), Brechbühler company; gradient 70–270 °C.

$[Mo(NO)(P\cap P)(NCMe)_2\mu\text{-}Cl_2][BAr^F{}_4]_2$ (1t and 1c): A solution of $[Mo(NO)(P\cap P)(NCMe)_3][BAr^F{}_4]$ (50 mg, 0.03 mmol) in chlorobenzene was heated at 120 °C for 30 min. The resulting solution was monitored by $^{31}P\{^1H\}$ NMR spectroscopy to ensure the completion of the reaction. The resulting mixture was filtered, and the solvents were evaporated to dryness. The obtained red oily residue was washed twice with pentane to remove the biphenyl side product, and finally a pure dinuclear isomeric mixture of **1t** and **1c** was obtained as a red solid in 92 % yield after drying in vacuo. ^1H NMR (500 MHz, C_6D_5Cl, 293 K): δ = 8.2 (s, $BAr^F{}_4$), 8.0 (m, Ph), 7.9 (m, Ph), 7.7 (m, Ph), 7.6 (s, $BAr^F{}_4$), 7.5 (m, Ph), 7.4–7.3 (m), 7.2–7.1 (m), 6.9 (m), 1.9 (s, CH_3, **1t**), 1.8 (s, CH_3, **1c**) ppm. $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_5Cl, 293 K): δ = 37.8 (d, $^2J_{P,P}$ = 108.7 Hz, **1t**), 27.1 (d, $^2J_{P,P}$ = 108.5 Hz, **1t**), 34.2 (d, $^2J_{P,P}$ = 109.3 Hz, **1c**), 29.9 (d, $^2J_{P,P}$ = 109.1 Hz, **1c**) ppm. $C_{140}H_{86}B_2Cl_2F_{48}Mo_2N_4O_4P_4$ (3208): calcd. C 52.41, H 2.70, N 1.75; found C 52.85, H 2.80, N 1.75. The presence of an isomeric mixture of **1c** and **1t** was confirmed by 1D NOE and ^{31}P COSY experiments.

$[Mo(NO)(P\cap P)(NCMe)_2\mu\text{-}Br_2][BAr^F{}_4]_2$ (2t and 2c): $[Mo(NO)(P\cap P)(NCMe)_3][BAr^F{}_4]$ (200 mg, 0.12 mmol) was dissolved in THF (10 mL) in Schlenk tube equipped with a Young tap, and 10 equiv. of C_6H_5Br (relative to the complex) was added into the THF solution. The resulting mixture was heated at 120 °C for 1 h. The reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy to ensure the completion of the reaction. After the completion of the reaction, the mixture was filtered, and the solvent was evaporated in vacuo. The obtained oily residue was washed with the minimum amount of pentane to remove the biphenyl-containing excess bromobenzene. Finally, a red dinuclear isomeric mixture of **2t** and **2c** was obtained in 84 % yield after drying in vacuo. ^1H NMR (400 MHz, [D$_8$]THF, 293 K): δ = 8.2 (m, ph), 8.0 (m, Ph), 7.8 (s, $BAr^F{}_4$), 7.7 (m, Ph), 7.6 (m, Ph), 7.5 (s, $BAr^F{}_4$) 7.2 (m), 7.0 (m), 2.4 (s, CH_3, **2t**), 2.3 (s, CH_3, **2c**) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, [D$_8$]THF, 293 K): δ = 37.4 (d, $^2J_{P,P}$ = 107.1 Hz, **2t**), 26.1 (d, $^2J_{P,P}$ = 107.1 Hz, **2t**), 33.8 (d, $^2J_{P,P}$ = 108.4 Hz, **2c**), 29.6 (d, $^2J_{P,P}$ = 108.4 Hz, **2c**) ppm.

$Mo(NO)(P\cap P)(CO)_2Cl$ (3): To a solution of $Mo(NO)(CO)_4(ClAlCl_3)$ (0.20 g, 0.49 mmol) in THF (15 mL) in a Schlenk tube equipped with a Young tap, a solution of DPEphos (0.265 g, 0.49 mmol) in THF (5 mL) was added. The resulting mixture was heated at 70 °C for 3 h. After the completion of the reaction, as indicated by $^{31}P\{^1H\}$ NMR spectroscopy, the red solution was filtered, and the solvent was evaporated to dryness. The solid residue was washed with pentane and then extracted with toluene. The concentrated toluene solution was layered with pentane to afford tiny yellow crystals of **3** after several days, yield (76 %, 280 mg). IR: $\tilde{\nu}$ = 1630 (NO), 2028(CO), 1957 (CO) cm^{-1}. ^1H NMR (500 MHz, CD_2Cl_2, 300 K): δ = 7.58 (Ph), 7.40 (m, Ph), 7.18 (m, Ph), 7.08 (m, Ph), 6.64 (m, DPEphos H) ppm. $^{31}P\{^1H\}$ NMR (125 MHz, CD_2Cl_2, 300 K): δ = 16.63 (s) ppm. $C_{38}H_{28}ClMoNO_4P_2$ (755.97): calcd. C 60.37, H 3.73, N 1.85; found C 60.42, H 3.92, N 1.68.

$[Mo(NO)(\kappa^3\text{-}P,P,O\text{-}DPEphos)Cl(PMe_3)]$ (4): $[Mo_2(NO)_2(P\cap P)_2Cl_4]\text{-}[\mu\text{-}Cl]_2$ (0.13 g, 0.084 mmol) was added to a stirred suspension of 1 % Na/Hg (10 mg, 0.42 mmol) in THF (5 mL) in a Schlenk tube with a Young tap, and PMe_3 (0.03 mL, 9 µL) was introduced with a syringe. The resulting solution was stirred for 6 h at room temperature. The resulting red solution was filtered, the solvent was removed in vacuo, and the residue was washed with pentane. The obtained red solid was extracted with toluene and then with benzene. The concentrated benzene solution of **4** was layered with pentane and kept in a fridge to afford pure red crystals of **4**, yield 50 %. IR: $\tilde{\nu}$ = 1546 (NO) cm^{-1}. ^1H NMR (400 MHz, C_6D_6, 300 K): δ = 7.5–7.44 (m, Ph), 7.35 (m, Ph), 7.22 (m, Ph), 7.01 (m, Ph), 6.8 (m, Ph) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 300 K): δ = 45 (dd, $^2J_{P,P}$ = 12.0 Hz), 26 (t, $^2J_{P,P}$ = 12.0 Hz) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 300 K): δ = 159.7 (d, J = 17.9 Hz, C_6H_4OP), 134 (m, Ph), 130 (s, Ph), 128 (m, Ph), 124 (s, C_6H_4OP), 118 (s, C_6H_4OP), 21 (m, CH_3) ppm. $C_{39}H_{37}ClMoNO_2P_3$ (776.05): calcd. C 60.36, H 4.81, N 1.80; found C 60.45, H 5.04, N, 1.62.

$[Mo(NO)(\kappa^3\text{-}P,P,O\text{-}DPEphos)Cl(PPh_3)]$ (5): $[Mo_2(NO)_2(P\cap P)_2Cl_4]\text{-}[\mu\text{-}Cl]_2$ (0.30 g, 0.195 mmol) and PPh_3 (0.102 g, 0.39 mmol) were added to a suspension of 1 % Na/Hg (22 mg, 0.96 mmol) in THF (10 mL). The resulting mixture was stirred overnight at room temperature. After the completion of the reaction, the red solution was filtered, the solvent was removed in vacuo, and the residue was washed with pentane. The crude product was extracted with toluene and then with benzene. The concentrated benzene solution was layered with pentane and kept at room temperature for several days to afford orange crystals of pure **5** in 55 % yield. IR: $\tilde{\nu}$ = 1561 (NO) cm^{-1}. ^1H NMR (400 MHz, C_6D_6, 300 K): δ = 8.2 (m, Ph), 7.86–7.76 (m, Ph), 7.73–7.68 (m, Ph), 7.40 (br s, Ph), 7.06–7.03 (m, Ph), 7.0–6.96 (m, Ph), 6.83–6.79 (m, DPEphos), 6.76–6.72 (m, DPEphos H), 6.68–6.64 (m, DPEphos H) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 300 K): δ = 75 (t, $^2J_{P,P}$ = 11.2 Hz, PPh_3), 45 (dd, $^2J_{P,P}$ = 165.3 Hz,

$^2J_{P,P}$ = 11.2 Hz, DPEphos), 39 (dd, $^2J_{P,P}$ = 165.3 Hz, $^2J_{P,P}$ = 11.22 Hz, DPEphos) ppm. $^{13}C^1H$ NMR (100.6 MHz, C_6D_6, 300 K): δ = 157 (m, Ph), 139 (d, $J_{C,P}$ = 35.8 Hz, Ph), 136 (s, Ph), 135 (d, $J_{C,P}$ = 34.6 Ph), 133 (s, Ph), 129 (m, Ph), 124 (m, DPEphos), 118 (m, DPEphos), 115 (m, DPEphos) ppm. $C_{54}H_{43}ClMoNO_2P_3$ (962.24): calcd. C 67.40, H 4.50, N 1.46; found C 66.96, H 5.09, N 1.15.

X-ray Diffraction Analyses: The single-crystal X-ray diffraction data were collected at 183(2) K with an Agilent Technologies Xcalibur Ruby area-detector diffractometer with a single-wavelength Enhance X-ray source with Mo-K_α radiation (λ = 0.71073 Å).[29] The selected suitable single crystals were mounted under polybutene oil on a flexible loop fixed to a goniometer head and transferred immediately to the diffractometer. The pre-experiment screening, data collection, data reduction, and analytical absorption correction[30] were performed with the CrysAlisPro program suite.[31] The structures were solved by direct methods by using SHELXS97.[32] The structure refinements were performed by full-matrix least-squares techniques on F^2 with SHELXL97.[32] PLATON[33] was used to check the results of the X-ray analysis. All programs used during the crystal-structure determination process are included in the WINGX software.[34] In the crystal structure of **2t**, two high residual peaks (greater than 5 e Å^3) were observed at chemically meaningless positions, near one benzene ring and one CF_3 group, in positions excluding disorders. These peaks are probably due to the flat platelet selected for the X-ray study, which showed monocrystallinity at ca. 80 %; the rest of the crystal consisted of multitwinned domains or intrusions, which prevented a postmeasurement twin refinement. For more details about the data collections and refinements parameters, see the crystallographic information files.[23]

CCDC 921398 (for **1t**), 1404271 (for **2t**), 921395 (for **3**), 921396 (for **4**), and 921397 (for **5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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Keywords: Redox chemistry · Reductive coupling · C–C coupling · Molybdenum · Phosphane ligands · Biaryls

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