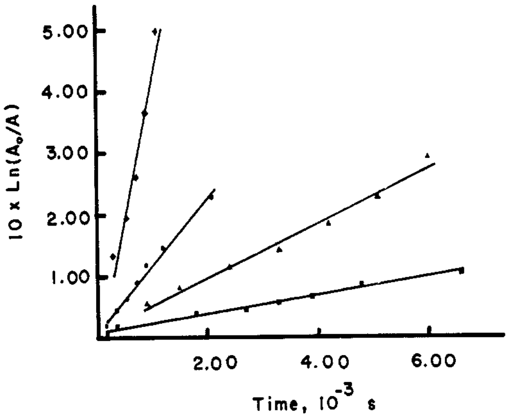

Figure 2. Plot of ln (A_0/A) vs. time for the decomposition 2 (R = n-C_9H_{19}) in cyclohexane solution: ◆, T = 75 °C; ●, T = 62 °C; ▲, T = 43 °C; ■, T = 30 °C.

Table II. Kinetic Parameters Associated with the Thermal Decomposition of 2[a]

temp, °C	$10^4 k_{obsd}$,[b,c] s^{-1}	E_a, kcal/mol	$\Delta S^{\ddagger}$, cal/(mol K)	log A
30	0.147 ± 0.005	15.1 ± 1.4	−29.7 ± 4.3	6.07
43	0.442 ± 0.002			
62	1.09 ± 0.05			
75	4.65 ± 0.05			

[a] See ref 10a. [b] $[2]_0$ = 0.50 M. [c] At 55 °C, the value of k_{obsd} showed only minor (ca. 10%) variation over the concentration range of [2] = 0.050–0.50 M.

product is iron pentacarbonyl, $Fe(CO)_5$ (48%). The rate of disappearance of 2, which can be conveniently monitored by infrared spectroscopy,[10a] obeys first-order kinetics for >2 half-lives and varies with temperature as shown in Figure 2. The same reaction performed under an atmosphere of CO (60 psi) yields only RC(O)R and RC(O)C(O)R.

The intra- vs. intermolecularity of the C–C bond-forming reactions was investigated by the use of crossover experiments. A sample containing a mixture of 50 mol % 2 and 50 mol % 1, R = CH_3, was allowed to decompose in cyclohexane at 62 °C and the product mixture examined by capillary GC/mass spectrometry.[10b] No crossover products were observed from which we conclude these coupling products are formed in processes which do not involve alkyl group scrambling and presumably occur by intramolecular pathways.

The activation parameters associated with the thermal decomposition of 2 are informative. In particular, the magnitude of the entropic term, $\Delta S^{\ddagger}$, is clearly inconsistent with a rate-determining step that involves an elementary unimolecular process in which two particles originate from one in the transition state.[11,12] However, similar entropies of activation are associated with at least two other well-defined unimolecular processes. Thus, the isomerization[13] of the dinuclear iron complex μ-$[(C_6H_5)(CH_3)Sn]_2Fe_2(CO)_8$ and the automerization of cyclobutadiene[14] exhibit an entropy of activation of −25 ± 5 and −25 ± 7 cal/(mol deg), respectively. In the former case, the purported rate-determining step involves the single scission of one of the bridging iron–tin bonds. In the latter instance it was concluded[15] that the abnormally low activation entropy associated with what is, in fact, a bondshifting reaction, reflects a reaction trajectory in which the extreme narrowness of the reaction barrier makes heavy-atom tunneling the dominant reaction pathway. Whether similar intramolecular processes are responsible for the unusually large negative entropy of reaction associated with the decomposition of 2 remains unknown.[16]

Collectively, the chemical behavior of 2 invites comparison to the process of oxidative addition, reductive elimination, ligand migration, and decarbonylation, all well-established reactions in the chemistry of mononuclear complexes. In fact, we cannot at present exclude the possibility that mononuclear species arise in a post-rate-limiting sequence leading to product-forming events. However, in part, the production of 1,2-diketones, which were not observed by Collman[17] in the decomposition of mononuclear iron complexes, mitigates against this possibility.

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(10) (a) Employing a calibrated, preheated, thermostated infrared cell (Foxboro/Analogs), the disappearance of the 2079-cm^{-1} band of a 0.5 M solution of 2 (R = n-C_9H_{19}) was monitored by FT-IR. (b) Under these conditions, the rate constant for the decomposition of 1, R = CH_3, is 1.36 × 10^{-4} s^{-1} while that of 2, R = n-C_9H_{19}, is 1.09 × 10^{-4} s^{-1}.

(11) (a) Benson, S. W. "Thermochemical Kinetics"; Wiley: New York, 1968; Chapter 3. (b) Benson, S. W.; O'Neal, H. E. "Kinetic Data on Gas Phase Unimolecular Reactions"; National Bureau of Standards: Washington, D.C., 1970.

(12) McCarthy, T. J.; Nuzzo, R. G.; Whitesides, G. M. *J. Am. Chem. Soc.* **1981**, *103*, 3396 and references therein.

(13) Grynkewich, G. W.; Marks, T. J. *Inorg. Chem.* **1976**, *15*, 1307.

(14) Whitman, D. W.; Carpenter, B. K. *J. Am. Chem. Soc.* **1982**, *104*, 6473.

(15) Carpenter, B. K. *J. Am. Chem. Soc.* **1983**, *105*, 1700.

(16) Classically, unimolecular isomerizations involving a one-particle transition state (i.e., a process in which one particle is transformed into one particle) are characterized by log A values ranging from ca. 11 to 14.[11b] Examples of other processes that exhibit abnormally low log A values have been cited elsewhere.[19]

(17) Collman, J. P. *Acc. Chem. Res.* **1975**, *8*, 342.

(18) Siegl, W. O.; Collman, J. P. *J. Am. Chem. Soc.* **1972**, *94*, 2516.

(19) Dewar, M. J. S.; Wade, L. E., Jr. *J. Am. Chem. Soc.* **1977**, *99*, 4417.

Synthesis of (Carbyne)metal Complexes by Oxide Abstraction from Acyl Ligands

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Summary: Stable carbyne complexes of the type *trans*-$X(CO)_2L_2M{\equiv}CR$ (M = Cr, Mo, W; R = C_6H_5, CH_3; X = Cl, Br, $CF_3C(O)O$, L_2 = 2 pyridine, tetramethylethylenediamine) are prepared in a single synthesis step by reaction of the respective acyl complexes $[NMe_4][(CO)_5MC(O)R]$ at low temperatures with $COCl_2$, $C_2O_2Cl_2$, $ClC(O)OCCl_3$, $C_2O_2Br_2$, or $(CF_3CO)_2O$ and subsequent addition of the nitrogenous ligands at warmer temperatures.

The chemistry of metal–carbon triple bonds has developed into an area of considerable interest. Metal alkylidyne, or carbyne, complexes are now established catalyst precursors for alkyne metathesis[1] and alkyne polymerization reactions.[2] Reactions of potential synthetic interest based on the coupling of carbyne and carbonyl ligands have been discovered.[3] Further exploration of this

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(1) Churchill, M. R.; Ziller, J. W.; Freudenberger, J. H.; Schrock, R. R. *Organometallics* **1984**, *3*, 1554–1562.

(2) Katz, T. J.; Ho, T. H.; Shih, N.-Y.; Ying, Y.-C.; Stuart, Van I. W. *J. Am. Chem. Soc.* **1984**, *106*, 2659–2668.

(3) Wolfgruber, M.; Sieber, W.; Kreissl, F. R. *Chem. Ber.* **1984**, *117*, 427–433.

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area of organometallic chemistry will be facilitated by the development of convenient and general methods for the preparation of carbyne metal complexes. Recently, we have demonstrated a new route to (alkylidyne)metal complexes by double β-addition of electrophiles to acetylide ligands.[4] We now wish to report a facile and highly efficient synthesis of carbyne complexes by formal abstraction of oxide from acyl ligands.

Abstraction of alkoxide from (alkoxycarbene)metal complexes is a widely used carbyne complex synthesis developed by Fischer and his group.[5] The requisite alkoxycarbene complex precursors are obtained by alkylation of acylmetal complexes.[6] A shorter one-step conversion of acyl complexes into carbyne complexes would require the formal abstraction of oxide, O^{2-}, from acyl ligands (eq 1). Such a transformation has been demonstrated by

$$[L_nM{-}C({=}O)R]^x \xrightarrow{-O^{2-}} [L_nM{\equiv}CR]^{x+2} \qquad (1)$$

Fischer in the reaction of $Li[(CO)_5WC(O)Ph]$ with phosphorous-based Lewis acids such as Ph_3PBr_2 which leads to $Br(CO)_4W{\equiv}CPh$ in moderate yield.[7] This reaction has not been developed further, but in principle it may represent an example of a general method.[8]

A particularly well-characterized class of carbyne complexes which can be obtained by alkoxide abstraction from alkoxycarbene complexes is comprised of trans-halo tetracarbonyl carbyne complexes $X(CO)_4M{\equiv}CR$ of chromium, molybdenum, and tungsten.[5] The usefulness of these compounds as a basis for general investigations into carbyne complex chemistry is somewhat limited by their thermolability. However, stable derivatives $X(CO)_2L_2M{\equiv}CR$ can be obtained by substitution of two carbonyl ligands with donor ligands such as phosphines or nitrogen heterocyclic compounds.[9] In order to have a convenient access to such stable disubstituted derivatives, we have developed a new synthetic method combining the advantages of direct conversion of acyl complexes into carbyne complexes with the benefits of stabilization of carbyne complexes by donor ligands.

Solutions of the tetramethylammonium salts of the anionic pentacarbonyltungsten acyl complexes **1** (**1a**, R = C_6H_5; **1b**, R = CH_3) in dichloromethane or tetrahydrofuran (THF) are cooled to low temperatures (**1a**, −70 °C; **1b**, −90 °C), and an equivalent amount or a slight excess of phosgene ($COCl_2$) is added. At these temperatures intermediates form, which upon warming to 0 °C cleanly transform into *trans*-chlorotetracarbonyltungsten carbyne complexes **2** (**2a**, R = C_6H_5; **2b**, R = CH_3) with concomitant evolution of gas (CO_2, CO) (eq 2). The carbyne complexes

$$\underset{\substack{\mathbf{1a},\ R\,=\,C_6H_5\\ \mathbf{1b},\ R\,=\,CH_3}}{[NMe_4][(CO)_5W{-}C(O)R]} \xrightarrow[\substack{-NMe_4Cl,\ -CO_2,\ -CO\\ CH_2Cl_2}]{COCl_2,\ \text{low temp}} \underset{\mathbf{2}}{Cl(CO)_4W{\equiv}CR} \qquad (2)$$

$$\underset{\mathbf{2}}{Cl(CO)_4W{\equiv}CR} \xrightarrow[-2CO]{\text{pyridine}} \underset{\mathbf{3}}{Cl(CO)_2(py)_2W{\equiv}CR} \qquad (3)$$

2 are not isolated, instead a fivefold excess of pyridine is added, and upon further warming to room temperature the bis(pyridine)-substituted complexes **3** form (eq 3). After chromatography at −20 °C on a short silica column with CH_2Cl_2/pentane (1:1) and recrystallization from CH_2Cl_2/pentane, the products are isolated in high yield (**3a**, 95%; **3b**, 85%).[10]

Table I

product[10]	reagent	yield, %
$Cl(CO)_2(py)_2W{\equiv}CPh$, **3a**	$COCl_2$	95
$Cl(CO)_2(py)_2W{\equiv}CMe$, **3b**	$COCl_2$	85
$Cl(CO)_2(TMEDA)W{\equiv}CPh$, **5**	$COCl_2$	95
5	$ClC(O)C(O)Cl$	95
$Br(CO)_2(TMEDA)W{\equiv}CPh$, **6**	$BrC(O)C(O)Br$	95
$Cl(CO)_2(bpy)W{\equiv}CPh$, **7**	$COCl_2$	94
$Cl(CO)_2(TMEDA)Cr{\equiv}CPh$, **8**	$ClC(O)OCCl_3$	93
$Cl(CO)_2(TMEDA)Mo{\equiv}CPh$, **9**	$ClC(O)OCCl_3$	95
$CF_3CO_2(CO)_2(TMEDA)W{\equiv}CPh$, **10**	$(CF_3CO)_2O$	78

[a] Initial reaction temperature is −78 °C except for preparation of **3b** (−90 °C). Solvent is CH_2Cl_2 or THF (**3a**, **10**).

The intermediate tetracarbonyl carbyne complexes **2** have been characterized by their known spectroscopic data.[11] If desired, these complexes can be isolated before the addition of pyridine. The low-temperature intermediates which form from the acyl complexes **1** and $COCl_2$ have not been characterized successfully. These species are postulated to be chloroformoxy-substituted carbene complexes $(CO)_5W{=}C[OC(O)Cl]R$, **4** (**4a**, R = C_6H_5; **4b**, R = CH_3). In agreement with this formulation is the reaction of **4a** with methanol leading to $(CO)_5W{=}C(OMe)Ph$, presumably via CO_2 loss from a further intermediate $(CO)_5W{=}C[OC(O)OMe]Ph$.[11] Also in support of **4a** is the formation of related acyloxy(phenyl)carbene complexes $(CO)_5W{=}C[OC(O)R']Ph$, from the reaction of **1a** with acyl halides R′COCl.[13]

The formal abstraction of oxide from acyl ligands can be achieved with a variety of other carbon-based Lewis acids. We have found that that trichloromethyl chloroformate (diphosgene) and oxalyl chloride can be used instead of phosgene. In addition, oxalyl bromide allows the synthesis of trans-bromo-substituted carbyne complexes. With trifluoroacetic anhydride as the Lewis acid, *trans*-η^1-trifluoroacetato-substituted carbyne complexes have been obtained. For all these reagents, the reaction conditions are similar to those described for the reaction with phosgene. These reagents can also be used for one-step syntheses of carbyne complexes of chromium and molybdenum starting from the respective pentacarbonylmetal acylates $NMe_4[(CO)_5MC(O)R]$. Tetramethylethylenediamine (TMEDA) is the preferred amine ligand for the isolation of chromium and molybdenum carbyne complexes. The increased stability of the TMEDA-substituted complexes allows their isolation as pure products without

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(4) Mayr, A.; Schaefer, K. C.; Huang, E. Y. *J. Am. Chem. Soc.* **1984**, *106*, 1517–1518.

(5) Fischer, E. O.; Schubert, U. *J. Organomet. Chem.* **1975**, *100*, 59–81.

(6) Fischer, E. O. *Angew. Chem.* **1974**, *86*, 651–663; *Adv. Organomet. Chem.* **1976**, *14*, 1–32.

(7) Fischer, H.; Fischer, E. O. *J. Organomet. Chem.* **1974**, *69*, C1–C3.

(8) A second example of this type of reaction is provided by the synthesis of $Cl(CO)_4W\ CNEt_2$ from $Li[(CO)_5WC(O)NEt_2]$ and $SOCl_2$ in 29% yield. Himmelrich, D.; Fischer, E. O. *Z. Naturforsch., B; Anorg. Chem., Org. Chem.* **1982**, *37B*, 1218.

(9) (a) Fischer, E. O.; Ruhs, A.; Kreissl, F. R. *Chem. Ber.* **1977**, *110*, 805–815. (b) Filippou, A.; Fischer, E. O. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1983**, *38B*, 587–591.

(10) Characteristic spectroscopic data (^{13}C NMR (ppm, $CDCl_3$): carbyne carbon (Cα) and carbonyl carbon (CO) and IR (cm^{-1}, CH_2Cl_2) of carbonyl ligands (ν_{CO}): **3a**, 263 (Cα), 220 (CO) and ν_{CO} 1985 (s), 1897 (s); **3b**, 274 (Cα), 220 (CO) and ν_{CO} 1982 (s), 1889 (s). **5**, 263 (Cα), 221 (CO) and ν_{CO} 1985 (s), 1892 (s); **6**, 263 (Cα), 221 (CO) and ν_{CO} 1984 (s), 1892 (s); **7**, 266 (Cα), 222 (CO) and ν_{CO} 1986 (s), 1899 (s); **8**, 298 (Cα), 231 (CO) and ν_{CO} 1994 (s), 1912 (s); **9**, 274 (Cα), 224 (CO) and ν_{CO} 1997 (s), 1912 (s); **10**, 274 (Cα), 221 (CO) and ν_{CO} 1987 (s), 1895 (s).

(11) Fischer, E. O.; Kreis, G. *Chem. Ber.* **1976**, *109*, 1673–1683.

(12) This type of intermediate may also be involved in the reaction of $NMe_4[(CO)_5MC(O)R]$ (M = Cr, Mo, W) with ClC(O)OMe which provides the methoxycarbene complexes $(CO)_5MC(OMe)R$ in high yields. Unpublished results.

(13) Fischer, E. O.; Selmayr, T.; Kreissl, F. R. *Chem. Ber.* **1977**, *110*, 2947–2955.

chromatography by simple recrystallization from CH_2Cl_2/pentane. All new carbyne complexes described in this work form stable crystalline compounds which can be handled without visible decomposition in air and at room temperature. Satisfactory analytical data have been obtained for all new compounds. The results are summarized in Table I.[14]

Substitution of two carbonyl ligands in the initial tetracarbonyl carbyne complexes is possible with a variety of ligands.[9] However, nitrogenous ligands have proven particularly useful for several reasons. The amine-substituted products form in very high yields, the products are stable enough for long-term storage, and at the same time a high degree of flexibility for further substitution reactions on the carbyne complexes is maintained. For example, reaction of the bis(pyridine)-substituted complexes **3** with bis(diphenylphosphino)ethane (dppe) gives the complexes $Cl(CO)_2(dppe)W{\equiv}CR$, **11**, (**11a**, R = C_6H_5; **11b**, R = CH_3) in high yields (**11a**, 95%; **11b**, 88%).[15] Reaction of **3** with PMe_3 leads to formation of $Cl(CO)_2(PMe_3)_2W{\equiv}CPh$, **12**, in 92% yield.[15,16]

With the described reactions, stable carbyne complexes of chromium, molybdenum, and tungsten are now easily accessible. This is particularly true for the molybdenum compounds which previously could be prepared only in low yields by established routes. The wide variety of complexes attainable will provide a convenient basis for future investigations into carbyne complex chemistry.

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[14] The carbyne complexes can also be obtained from the lithium salts of the acyl complexes. This way, one-pot syntheses starting from the metal hexacarbonyls are possible; however, more extensive workup procedures due to concomitant metal hexacarbonyl are necessary.

[15] ^{13}C NMR (ppm, $CDCl_3$) and IR (cm^{-1}, CH_2Cl_2): **11a**, 267 (Cα), 213 (CO) and ν_{CO} 2003 (s), 1937 (s); **11b**, 279 (Cα), 213 (CO) and ν_{CO} 2001 (s), **12**, 266 (Cα), 212 (CO) and ν_{CO} 2000 (s), 1926 (s). The ^{13}C resonances in **11** and **12** are multiplets due to coupling with the phosphine ligands. The centers of the multiplets are given as values.

[16] Complex **12** cannot be prepared from the tetracarbonyl carbyne complex directly due to attack of PMe_3 at the carbyne carbon in $X(CO)_4WCR$. See ref 6a.

Heteronuclear Intervalent Electron Transfer in Organometallic Complexes

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Summary: Intramolecular metalation of [(dimethylamino)methyl]ferrocene with palladium chloride gives compound **2** from which the complexes **3** and **4** can be prepared. In every case, oxidation of the iron center gives an Fe(III)–Pd(II) compound which exhibits a near-infrared band for heterometal electron transfer. The band energy is dependent on the ligand L in **3**.

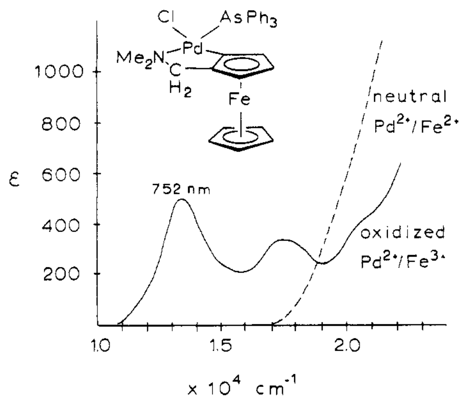

Figure 1. Near-infrared and visible spectrum of **3** (L = $AsPh_3$) before and after electrochemical oxidation at the iron center.

Numerous examples of mixed-valence organometallic compounds have been reported, but they have been limited almost entirely to compounds having two or more ferrocenyl groups, intervalent transfer being observed between Fe(II) and Fe(III).[2] With the exception of bis(fulvalene)diiron, all of the mixed-valence ferrocenyl-containing compounds described thus far are found in Hush's class II,[3] compounds with weak interaction between iron sites.

More recently, we and others have described three types of heterometal organometallic compounds that exhibit intramolecular electron transfer.[4-7] In each case, one site was a ferrocenyl group while the other was a ruthenium or cobalt ion. Unfortunately, none of these systems is amenable to significant extension, and it has been one of our goals to find organometallic mixed-valence systems within which one can make many derivatives to explore better the nature of heteronuclear intervalent electron transfer. We now wish to communicate our initial results on such a system.

If $FcCH_2NMe_2$ is allowed to react directly with $[PdCl_4]^{2-}$, complex **1** is formed,[8,9] while intramolecular metalation occurs to give **2** in the presence of a base such as sodium acetate.[10,11] The halide bridge of **2** is broken with a slight excess of ligand L (= phosphine, phosphite, pyridine, etc.) to give **3** (or **4** if L is a bidentate phosphine and $TlPF_6$ is added to precipitate the displaced Cl^-; Scheme I). The chloride ligand in **3** can be replaced in an exchange reaction. A few of the compounds synthesized thus far are given in Table I along with data pertinent to their electron-transfer properties.[12]

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[1] Exchange visitor from Fuzhou University, Fuzhou, Fujian, People's Republic of China, 1982–1983.

[2] See, for example: (a) Powers, M. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 4393. (b) Kramer, J. A.; Hendrickson, D. N. *Inorg. Chem.* **1980**, *19*, 3330.

[3] Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391.

[4] Colbran, S. B.; Robinson, B. H.; Simpson, J. *Organometallics* **1983**, *2*, 945, 952.

[5] Dowling, N.; Henry, P. M.; Lewis, N. A.; Taube, H. *Inorg. Chem.* **1981**, *20*, 2345.

[6] Dowling, N.; Henry, P. M. *Inorg. Chem.* **1982**, *21*, 4088.

[7] Kotz, J.; Neyhart, G.; Vining, W. J.; Rausch, M. D. *Organometallics* **1983**, *2*, 79.

[8] Fc is an abbreviation used throughout for the ferrocenyl group $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$ or $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3)$.

[9] Moynahan, E. B.; Popp, F. D.; Werneke, M. F. *J. Organomet. Chem.* **1969**, *19*, 229.

[10] Sokolov, V. I.; Troitskaya, L. L.; Reutov, O. A. *J. Organomet. Chem.* **1979**, *182*, 537.

[11] Gaunt, J. C.; Shaw, B. L. *J. Organomet. Chem.* **1975**, *102*, 511.

[12] The complexes were all prepared in good yield according to the literature (see ref 9 and 11). Except for L = $P(OEt)_3$, X = Cl and L = PPh_3, X = I or SCN, all were analyzed for C and H (and N in some cases), and all analyses were acceptable. The unanalyzed complexes all displayed cyclic voltammograms with no visible impurities, and all gave the correct number of coulombs for a one-electron process on exhaustive anodic electrolysis. The complex with L = PPh_3 and X = SCN is thought to have an S-bonded thiocyanate ligand since the C–N stretching band (at 2087 cm^{-1}) was appropriate for an S-bonded ligand.

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