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Unprecedented Allenylidene Transfer from Chromium to Tungsten

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Pyrimidylallenylidene complexes **1** ($[(CO)_5M{=}C{=}C{=}\overline{C(NC_3H_3N}Et)]$; M = Cr (**a**), W (**b**)) were prepared in a one-pot procedure from readily available 2-ethynylpyrimidine, butyllithium, $[(CO)_5M(THF)]$, and triethyloxonium tetrafluoroborate. In addition to **1a**,**b**, the homobinuclear allenylidene complexes **2a**,**b** ($[(CO)_5M{=}C{=}C{=}\overline{C(NC_3H_3N}Et)M(CO)_5]$; M = Cr, W) were formed. In **2a**,**b** the second $(CO)_5M$ moiety is attached to the nonalkylated nitrogen atom of the pyrimidyl ring. Treatment of the *chromium* complex **1a** with an excess of $[(CO)_5W(THF)]$ afforded the *tungsten* allenylidene complex **2b** by transmetalation of the allenylidene ligand and addition of $(CO)_5W$. The allenylidene ligands of other chromium allenylidene complexes $[(CO)_5Cr{=}C{=}C{=}C(R^1)R^2]$ could likewise be transferred to tungsten. In contrast, the reverse transmetalation from *tungsten* to *chromium* could not be achieved. DFT calculations indicate that the reaction proceeds by an associative rather than a dissociative pathway. The initiating reaction step is coordination of a $(CO)_5W$ fragment to the $C_\alpha{-}C_\beta$ bond of the allenylidene ligand.

Introduction

The first planned synthesis of stable heteroatom-stabilized carbene complexes, $[L_nM{=}C(XR)R']$ (Fischer carbene complexes), was published in 1964.[1] Since then, this class of compounds has evolved into very important and useful synthetic tools in organic synthesis.[2] One of the very first reactions to be explored was the transfer of carbene ligands to olefins to form cyclopropanes (cyclopropanation).[3] From the results of a detailed study using a chiral carbene(carbonyl)phosphane complex, it was concluded that free carbenes can be excluded as reaction intermediates.[4] Thermolysis of carbene complexes at elevated temperatures led to dimerization of the carbene ligands, giving symmetrical olefins.[5] A mechanistic study confirmed that again free carbenes are not involved in the dimerization process.[5d] In the presence of palladium acetate the dimerization proceeded quickly at or even below ambient temperature.[6] The transfer of a carbene ligand to palladium seems likely.

The stoichiometric transfer of carbene ligands from chromium or tungsten pentacarbonyl carbene complexes to other metal centers such as gold,[7] iron,[8] nickel,[8] cobalt,[9] copper,[10] rhodium,[11] or palladium[12] has likewise been reported. In all of these reactions free carbenes can be excluded as reaction intermediates. Very likely, the transfer proceeds via heterobimetalic intermediates.

In recent years, the catalytic transfer of the carbene ligand from group 6 carbene complexes to another metal center is gaining considerable interest since this reaction mode opens up new applications for Fischer carbene complexes.[13]

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[1] Fischer, E. O.; Maasböl, A. *Angew. Chem.* **1964**, *76*, 645; *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 580.

[2] Reviews: (a) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissl, R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Deerfield Beach, FL, 1983. (b) Dötz, K. H. *Angew. Chem.* **1984**, *96*, 573; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. (c) Wulff, W. D. In *Comprehensive Organic* Synthesis; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 5, p 1065. (d) Schwindt, M. A.; Miller, J. R.; Hegedus, L. S. *J. Organomet. Chem.* **1991**, *413*, 143. (e) Rudler, H.; Audouin, M.; Chelain, E.; Denise, B.; Goumont, R.; Massoud, A.; Parlier, A.; Pacreau, A.; Rudler, M.; Yefsah, R.; Alvarez, C.; Delgado-Reyes, F. *Chem. Soc. Rev.* **1991**, *20*, 503. (f) Grotjahn, D. B.; Dötz, K. H. *Synlett.* **1991**, 381. (g) Wulff, W. D. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 12, p 470. (h) Hegedus, L. S. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 12, p 549. (i) Harvey, D. F.; Sigano, D. M. *Chem. Rev.* **1996**, *96*, 271. (j) Hegedus, L. S. *Tetrahedron* **1997**, *53*, 4105. (k) Aumann, R.; Nienaber, H. *Adv. Organomet.* Chem. **1997**, *41*, 163. (l) Alcaide, B.; Casarrubios, L.; Domínguez, G.; Sierra, M. A. *Curr. Org. Chem.* **1998**, *2*, 551. (m) Sierra, M. A. *Chem. Rev.* **2000**, *100*, 3591. (n) de Meijere, A.; Schirmer, H.; Duetsch, M. *Angew. Chem.* **2000**, *112*, 4124; *Angew. Chem., Int. Ed.* **2000**, *39*, 3964. (o) Barluenga, J.; Flórez, J.; Fañanás, F. J. *J. Organomet. Chem.* **2001**, *624*, 5.

[3] (a) Fischer, E. O.; Dötz, K. H. *Chem. Ber.* **1970**, *103*, 1273. (b) Dötz, K. H.; Fischer, E. O. *Chem. Ber.* **1972**, *105*, 1356. (c) Fischer, E. O.; Dötz, K. H. *Chem. Ber.* **1972**, *105*, 3966. (d) The formation of a cationic carbene complex $[Cp(CO)_2Fe{=}CH_2]^+$ as an intermediate in the reaction of $[Cp(CO)_2Fe{-}CH_2OMe$ with acids in the presence of cyclopentene to give norcarane was proposed in 1966: Jolly, P. W.; Pettit, R. J. *Am. Chem. Soc.* **1966**, *88*, 5044.

[4] Cooke, M. D.; Fischer, E. O. *J. Organomet. Chem.* **1973**, *56*, 279.

[5] (a) Fischer, E. O.; Heckl, B.; Dötz, K. H.; Müller, J.; Werner, H. *J. Organomet. Chem.* **1969**, *16*, P29. (b) Fischer, E. O.; Dötz, K. H. *J. Organomet. Chem.* **1972**, *36*, C4. (c) Fischer, E. O.; Plabst, D. *Chem. Ber.* **1974**, *107*, 3326. (d) Casey, C. P.; Anderson, R. L. *J. Chem. Soc., Chem. Commun.* **1975**, 895.

[6] (a) Sierra, M. A.; Mancheño, M. J.; Sáez, E.; del Amo, J. C. *J. Am. Chem. Soc.* **1998**, *120*, 6812. (b) Sierra, M. A.; Amo del, J. C.; Mancheno, M. J.; Gómez-Gallego, M. *J. Am. Chem. Soc.* **2001**, *123*, 851.

[7] (a) Aumann, R.; Fischer, E. O. *Chem. Ber.* **1981**, *114*, 1853. (b) Fischer, E. O.; Böck, M.; Aumann, R. *Chem. Ber.* **1983**, *116*, 3618. (c) Fischer, E. O.; Böck, M. *Monatsh. Chem.* **1984**, *115*, 1159. (d) Fischer, E. O.; Böck, M. *J. Organomet. Chem.* **1985**, *287*, 279.

[8] Fischer, E. O.; Beck, H.-J. *Angew. Chem.* **1970**, *82*, 44; *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 72.

[9] Jordi, L.; Moretó, J. M.; Ricart, S.; Viñas, J. M. *Organometallics* **1992**, *11*, 3507.

[10] (a) Straub, B. F.; Hofmann, P. *Angew. Chem.* **2001**, *113*, 1328; *Angew. Chem., Int. Ed.* **2001**, *40*, 1288. (b) Barluenga, J.; López, L. A.; Löber, O.; Tomás, M.; García-Granda, S.; Alvarez-Rúa, C.; Borge J. *Angew. Chem.* **2001**, *113*, 3495; *Angew. Chem., Int. Ed.* **2001**, *40*, 3392.

[11] Barluenga, J.; Vicente, R.; López, L. A.; Rubio, E.; Tomás, M.; Álvarez-Rúa, C. *J. Am. Chem. Soc.* **2004**, *126*, 470.

[12] (a) Liu, S.-T.; Hsieh T.-Y.; Lee, G.-H.; Peng, S.-M. *Organometallics* **1998**, *17*, 993. (b) Ku, R.-Z.; Huang, J.-C.; Cho, J.-Y.; Kiang, F.-M.; Reddy, K. R.; Chen, Y.-C., Lee, K.-J.; Lee, J.-H.; Lee, G.-H.; Peng, S.-M.; Liu, S.-T. *Organometallics* **1999**, *18*, 2145. (c) Albéniz, A. C.; Espinet, P.; Manrique, R.; Pérez-Mateo, A. *Angew. Chem.* **2002**, *114*, 2469; *Angew. Chem., Int. Ed.* **2002**, *41*, 2363.

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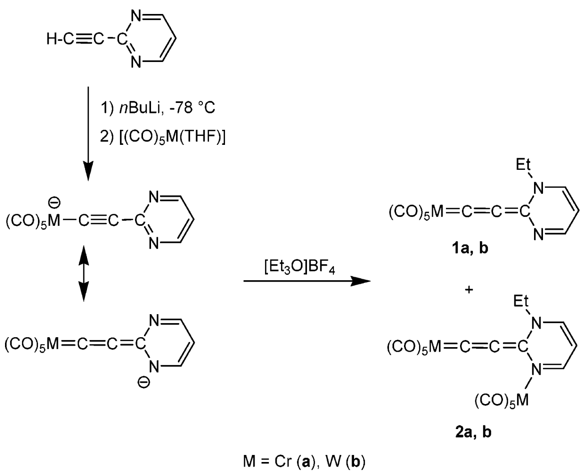
Vinylidene and allenylidene complexes may be regarded as unsaturated carbene complexes. They have found application in the field of stoichiometric organic synthesis[14] as well as in catalysis.[15] Due to their versatile chemical and physicochemical properties, these compounds are also discussed as potential precursors for applications in the field of material science for instance as molecular wires,[16] as liquid crystals,[17] and for nonlinear optics.[18] The transfer of a vinylidene ligand from manganese to rhenium[19] and from rhodium to iridium has been described.[20] In contrast to group 6 carbene complexes and to these vinylidene complexes the transfer of allenylidene ligands from chromium, molybdenum, and tungsten to another transition metal center has not been observed, although the thermal dimerization of the allenylidene ligand in $[Cp(CO)_2Mn{=}C{=}C{=}C(t\text{-}Bu)_2]$[21] and the photochemically induced dimerization of that in $[(CO)_5Cr{=}C{=}C{=}CPh_2]$[22] has been described. We now report the first examples of transmetalation of allenylidene ligands from chromium to tungsten.

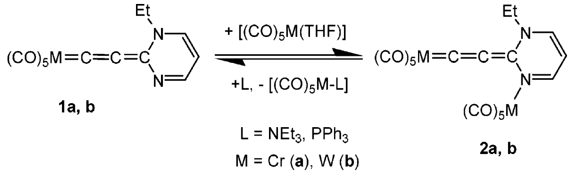
Results and Discussion

Preparative Results. Deprotonation of 2-ethynylpyrimidine with *n*-butyllithium at −78 °C and reaction with the solvent complexes $[(CO)_5M(THF)]$ (M = Cr, W) followed by alkylation of the resulting alkynyl metalates with triethyloxonium tetrafluoroborate affords the pyrimidyl-terminated allenylidene complexes **1a** and **1b** (Scheme 1) in a simple one-pot synthesis. The reaction sequence has recently been introduced for the synthesis of *N*-stabilized allenylidene complexes.[23] Surprisingly, in addition to the mononuclear complexes **1a** and **1b** expected on the basis of previous results, the homobinuclear complexes **2a** and **2b** are likewise formed. In **2a** and **2b** the “second” $(CO)_5M$ moiety is bonded to the pyrimidyl ring via the nonalkylated nitrogen atom. The ratio **1a**/**2a** (**1b**/**2b**) depends on the reaction conditions and generally decreases with increasing excess of $[(CO)_5M(THF)]$. When $[(CO)_5W(THF)]$ is used in a 3-fold excess, complex **2b** is the only product. In contrast, when a 3-fold excess of $[(CO)_5Cr(THF)]$ is employed in the reaction with deprotonated 2-ethynylpyrimidine, the yield of the binuclear complex **2a** is still low presumably due to steric congestion and to a higher stability of the tungsten complex when compared with the corresponding chromium compound.

Scheme 1



Scheme 2



The binuclear complexes **2a** and **2b** very likely are formed either (a) by addition of $[(CO)_5M(THF)]$ to the alkynyl metalate followed by alkylation or (b) by alkylation of the alkynyl metalate followed by addition of $[(CO)_5M(THF)]$ to **1a**,**b**. The latter sequence is supported by the fact that on treatment of **1a** or **1b** with $[(CO)_5M(THF)]$ the binuclear complexes **2a** and **2b** are formed. A full conversion to **2b** is already achieved when $[(CO)_5W(THF)]$ is used in 2-fold excess in the reaction with **1b**. In contrast, the analogous reaction of the chromium complex **1a** with $[(CO)_5Cr(THF)]$ affords **2a** in only 41% yield, even when 5 equiv of $[(CO)_5Cr(THF)]$ is used.

In turn, the addition of Lewis bases L (e.g., L = Et_3N or PPh_3) gives rise to the formation of **1a**,**b** from **2a**,**b** (Scheme 2). The elimination of the *N*-bound $(CO)_5M$ fragment as amine or phosphane complex $[(CO)_5M{-}L]$ is much faster for the chromium compound **2a** than for the tungsten complex **2b**. When a solution of **2a** is treated with 1.1 equiv of L, the mononuclear complex **1a** is quantitatively formed within 30 min. The corresponding reaction of **2b** requires 4 h. Selective oxidation of **2a**,**b** by stirring solutions of the complexes in air also yields **1a**,**b**. In addition $[M(CO)_6]$ and some unidentified decomposition products are formed.

Addition of $(CO)_5M$ to the nitrogen atom leads to a shift of the ν(CCC) absorption toward shorter wavenumbers by 23−24 cm^{-1}, indicating a less pronounced contribution of the dipolar iminium-alkynyl resonance form **II** (Scheme 3) to the overall bond description in **2a**,**b** when compared to **1a**,**b**. In accord with the enhanced contribution of the cumulene resonance form **I** is (a) the shift toward lower energy of the metal-to-ligand charge-transfer absorption at longest wavelength in the UV−vis

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(13) (a) Göttker-Schnetmann, I.; Aumann, R. *Organometallics* **2001**, *20*, 346. (b) Aumann, R.; Göttker-Schnetmann, I.; Fröhlich, R.; Meyer, O. *Eur. J. Org. Chem.* **1999**, *2545*. (c) Göttker-Schnetmann, I.; Aumann, R.; Bergander, K. *Organometallics* **2001**, *20*, 3574. (d) Sakurai, H.; Tanabe, K.; Narasaka, K. *Chem. Lett.* **1999**, 75. (e) Wang, H. M. J.; Lin, I. J. B. *Organometallics* **1998**, *17*, 972. (f) Barluenga, J.; Vicente, R.; Barrio, P.; López, L. A.; Tomás, M. *J. Am. Chem. Soc.* **2004**, *126*, 5974.

(14) For reviews see: (a) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59. (b) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197. (c) Doherty, S.; Corrigan, J. F.; Carty, A. J.; Sappa, E. *Adv. Organomet. Chem.* **1995**, *37*, 39. (d) Werner, H. *J. Chem. Soc., Chem. Commun.* **1997**, 903. (e) Bruce, M. I. *Chem. Rev.* **1998**, *98*, 2797. (f) Touchard, D.; Dixneuf, P. H. *Coord. Chem. Rev.* **1998**, *178*−*180*, 409. (g) Cardierno, V.; Gamasa, M. P.; Gimeno, J. *Eur. J. Inorg. Chem.* **2001**, 571. (h) Rigaut, S.; Touchard, D.; Dixneuf, P. H. *Coord. Chem. Rev.* **2004**, *248*, 1585. (i) Cadierno, V.; Gamasa, M. P.; Gimeno, J. *Coord. Chem. Rev.* **2004**, *248*, 1627.

(15) For recent reviews see: (a) Bruneau, C.; Dixneuf, P. H. *Acc. Chem. Res.* **1999**, 32, 311. (b) Bruneau, C.; Dixneuf, P. H. *Angew. Chem.* **2006**, *118*, 2232; *Angew. Chem. Int. Ed.* **2006**, *45*, 2176.

(16) Recent reviews: (a) Bunz, U. H. F. *Angew. Chem.* **1996**, *108*, 1047; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 969. (b) Paul, F.; Lapinte, C. *Coord. Chem. Rev.* **1998**, *178*−*180*, 431.

(17) (a) Hudson, S. A.; Maitlis, P. M. *Chem. Rev.* **1993**, *93*, 861. (b) Giroud-Goquin, A. M.; Maitlis, P. M. *Angew. Chem.* **1991**, *103*, 370; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 375.

(18) Recent reviews: (a) Long, N. J. *Angew. Chem.* **1995**, *107*, 37; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 21. (b) Barlow, S.; O’Hare, D. *Chem. Rev.* **1997**, *97*, 637.

(19) Kolobova, N. E.; Antonova, A. B.; Khitrova, O. M. *J. Organomet. Chem.* **1978**, *146*, C17.

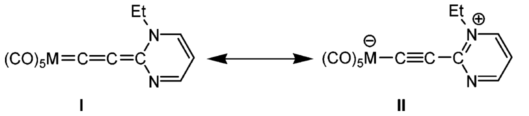
(20) Höhn, A.; Otto, H.; Dziallas, M.; Werner, H. *J. Chem. Soc., Chem. Commun.* **1987**, 852.

(21) Berke, H. *Angew. Chem.* **1976**, *88*, 684; *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 624.

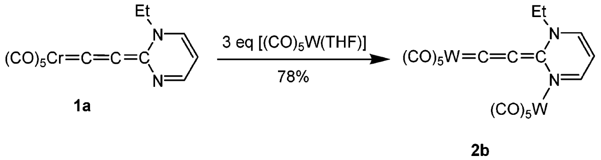
(22) Abd-Elzaher, M. M.; Weibert, B.; Fischer, H. *Organometallics* **2004**, *24*, 1050.

(23) Fischer, H.; Szesni, N.; Roth, G.; Burzlaff, N. Weibert, B. *J. Organomet. Chem.* **2003**, *683*, 301.

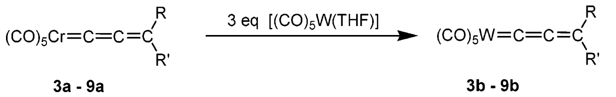
Scheme 3



Scheme 4



Scheme 5



M = Cr (**a**), W (**b**)

	3	4	5	6	7	8	9
R	NMe_2	NMe_2	NMe_2	N(Me)Et	N(Me)Bu	NPh_2	$C_6H_4NMe_2$-p
R'	NMe_2	OMe	Ph	Ph	Ph	OMe	$C_6H_4NMe_2$-p
Yield	92%	97%	96%	86%	92%	93%	83%

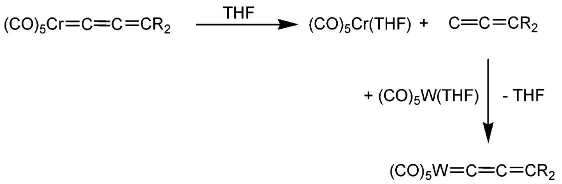
spectrum and (b) the downfield shift of the allenylidene C_α atom in the ^{13}C NMR spectrum (by about 30 ppm) upon coordination of the metal fragment to the pyrimidyl nitrogen atom.

Attempts to prepare *hetero*binuclear complexes provided surprising results. When 3 equiv of $[(CO)_5W(THF)]$ was added to a solution of the chromium complex **1a** at ambient temperature, instead of a *hetero*binuclear complex the *homo*binuclear tungsten allenylidene complex **2b** was isolated from the reaction mixture as the only product in 78% yield (Scheme 4). Obviously, besides coordination of the $W(CO)_5$ fragment to the nonalkylated nitrogen atom the allenylidene ligand had also been transferred from chromium to tungsten. To the best of our knowledge, transmetalation of allenylidene ligands is unprecedented. The reverse, transmetalation of the allenylidene ligand from tungsten to chromium by reaction of $[(CO)_5Cr(THF)]$ with **1b**, has not been observed. When employing the same reaction conditions, the transfer of the allenylidene ligand from tungsten or chromium to $[(CO)_5Mo(THF)]$, [(COD)CuCl], $[(PhCN)_2PdCl_2]$, or $[(COD)PtCl_2]$ has likewise not been observed.

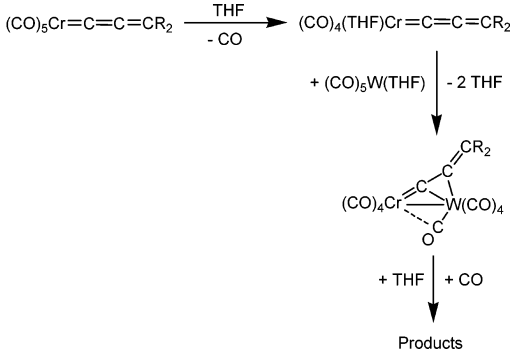
However, the transmetalation of an allenylidene ligand is not confined to pyrimidyl-terminated allenylidene ligands. Treatment of the aminoallenylidene chromium complexes **3a**−**8a** with $[(CO)_5W(THF)]$ gave the tungsten complexes **3b**−**8b** in isolated yields ranging from 86 to 97%. Diarylallenylidene ligands were also transferrable from chromium to tungsten (Scheme 5). At ambient temperature all reactions were complete within 3 h.

It was in neither one of these reactions possible to convert the tungsten complexes **3b**−**9b** back to their chromium analogues **3a**−**9a**. When the complexes **6a** and **7a** were employed, the *E/Z* ratio of isomers (due to the relative orientation of the *N*-bound substituents) did not change during the course of the reaction. The formation of allenylidene dimers, hexapentaenes, has not been observed. Therefore, free allenylidenes as reaction intermediates could be excluded. Note that photolysis of $[(CO)_5Cr{=}C{=}C{=}CPh_2]$ in pentane/dichloromethane at −30 °C afforded tetraphenylhexapentaene in 83% yield.[22] The high-yield formation of **9b** indicates that initial coordination of the tungsten pentacarbonyl fragment to a C_γ-bound nitrogen atom (as in complexes **2**) is not a prerequisite for the transmetalation to occur.

Scheme 6



Scheme 7



The thermally induced transmetalation of the carbene ligand in pentacarbonyl oxacyclopentylidene chromium to $[W(CO)_6]$ has been reported by Casey et al.[5d] When the carbene complex $[(CO)_5Cr{=}C(NMe_2)Ph]$,[24] having the same substitution pattern as allenylidene complex **5a**, was treated with $[(CO)_5W(THF)]$, no reaction was observed. This observation emphasizes the importance of the unsaturated chain for the transmetalation.

Reaction Mechanism and DFT Calculations. Several pathways for the transmetalation reaction are conceivable. The reaction can proceed by either a dissociative or an associative mechanism. In dissociative pathways the reaction is initiated either by a Cr−allenylidene or Cr−CO bond rupture. Cr−allenylidene dissociation and generation of free allenylidenes (Scheme 6) is unlikely due to the high Cr−allenylidene bond dissociation energy ($[(CO)_5Cr{=}C{=}C{=}CMe_2]$: 283 kJ/mol; ($[(CO)_5Cr{=}C{=}C{=}C(NMe_2)_2]$: 265 kJ/mol; $[(CO)_5Cr{=}C{=}C{=}CH_2]$: 283 kJ/mol[25]). Such a mechanism is also not in accord with the experimental results (see above). Furthermore, examples of free allenylidenes are very scarce.[26]

The alternative dissociative mechanisms involves initial and rate-determining Cr−(*cis*-CO) dissociation followed by reaction of the resulting allenylidene tetracarbonyl complex with $[(CO)_5W(THF)]$ to give a binuclear allenylidene-bridged $(CO)_4Cr-W(CO)_5$ complex. Related vinylidene-bridged homobinuclear dichromium complexes have been prepared and structurally characterized.[27] Subsequent rearrangement and reaction with THF and/or CO would afford the final products (Scheme 7).

The lower bond dissociation energy of Cr−CO (148 kJ/mol) compared to that of Cr−allenylidene (277 kJ/mol) would favor such an initiating step. Cr−CO dissociation followed by carbene transfer was also proposed to account for the experimental data in the dimerization of the carbene ligand of pentacarbonyl oxacyclopentylidene chromium.[5d] However, for the Cr → W transmetalation such a reaction sequence is not compatible with the concentration dependence of the reaction. Diluting the solutions considerably reduces the reaction rate. In addition,

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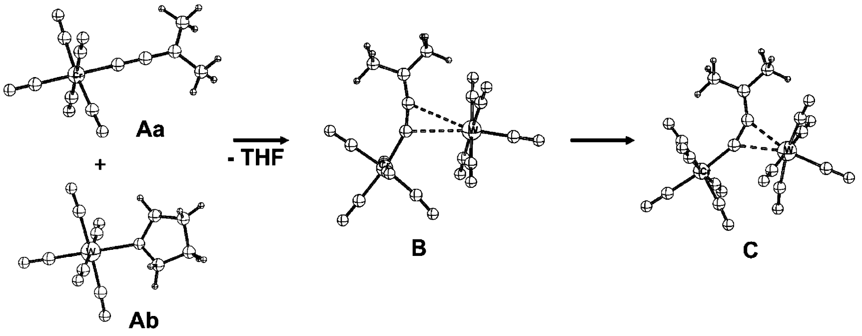
[24] Fischer, E. O.; Leupold, M. *Chem. Ber.* **1972**, *105*, 599.

[25] Re, N.; Sgamellotti, A.; Floriani, C. *Organometallics* **2000**, *19*, 1115.

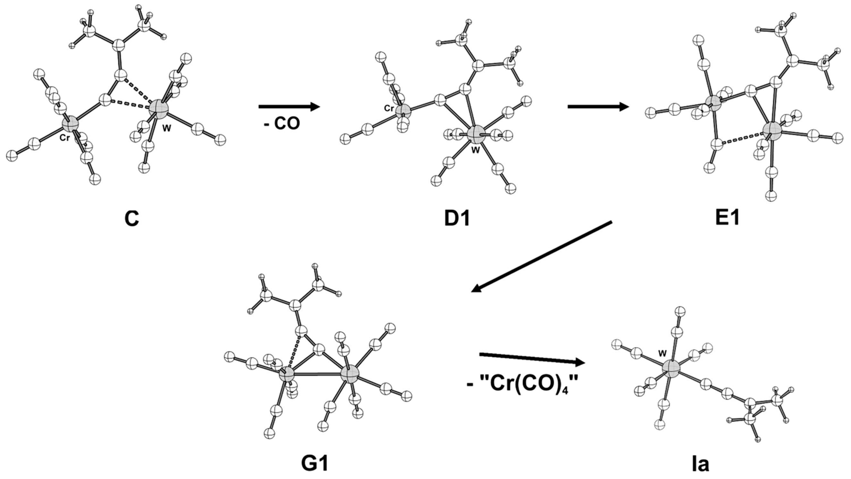
[26] (a) Stang, P. J. *Acc. Chem. Res.* **1982**, *15*, 348. (b) Huntsman, W. D. in The chemistry of ketenes, allenes, and related compounds (Ed. Patai, S.), Wiley, Chichester, 1980, p 521.

[27] Karl, C. C.; Joneleit, S.; Abd-Elzaher, M.; Weibert, B.; Fischer, H. *J. Organomet. Chem.* **2003**, *677*, 46.

Scheme 8



Scheme 9



lower yields than those observed (83−97%, Scheme 5) would have been expected since [(CO)$_5$W(THF)] rapidly reacts with free CO to form hexacarbonyl tungsten.

Therefore, an associative mechanism is more likely and is indicated by the pronounced concentration dependence. DFT calculations were performed using [(CO)$_5$Cr=C=C=CMe$_2$] (**Aa**) as the model allenylidene complex. Three associative pathways were considered in detail. All three have the first reaction step(s) in common initiated by an electrophilic addition of "W(CO)$_5$" (after dissociation of THF from [(CO)$_5$W(THF)] (**Ab**)) to [(CO)$_5$Cr=C=C=CMe$_2$]. The HOMO in [(CO)$_5$Cr=C=C=CMe$_2$] is an in-plane orbital composed of contributions from the carbonyl-chromium fragment, C_β, and C_α of the allenylidene ligand. Therefore, the first step is an in-plane coordination of "W(CO)$_5$" to the C_α−C_β bond to form via **B** the heterobinuclear complex **C** (Scheme 8). As a consequence of the interaction, the originally linear CCC fragment is bent and the Cr−C distance as well as the CC distances are sightly elongated. Related homobinuclear μ:η^1,η^2-vinylidene and μ:η^1,η^2-allenylidene complexes [Cp(CO)$_2$Mn]$_2$(C=CR$_2$) (CR$_2$ = C(Ph)-C$_4$H$_8$OMe, C=CMe$_2$, C=C(CH$_2$)$_5$) have been isolated and structurally characterized.[28,29]

The overall Gibbs free energy for the formation of **C** (+ THF) is +28.5 kJ/mol. The transition state **B** (+ THF) for the coordination reaction is 87.2 kJ/mol higher in energy than the starting complexes **Aa** and **Ab** and essentially results from W−THF bond dissociation and bending of the CCC fragment.

Starting from **C** three different pathways are conceivable.

Pathway 1. One Cr−(*cis*-CO) bond dissociation energy in **C** is calculated to be considerably less than in **Aa** (106 versus 148 kJ/mol). Therefore, a mechanism involving CO dissociation from **C** seems possible (Scheme 9). As a consequence of elongating the Cr−CO bond closest to the tungsten atom, the Cr−C−C angle increases, the Cr−W distance decreases, and a *cis*-CO ligand from tungsten migrates to chromium. In intermediate **E1** the Cr−W distance is 3.07 Å and corresponds to a Cr−W single bond. For comparison the W−W bond in, for example, [(CO)$_5$W]$_2$(μ-C(Ph)H) is 3.118(1) Å,[30] and the Cr−Cr distance in the vinylidene-bridged complex [(CO)$_5$Cr(μ-η^1,η^2-C=CMe$_2$)Cr(CO)$_4$] is 3.000(1) Å.[27] The "migrating" CO occupies a bridging position, but is closer to chromium than to the tungsten atom. However, this Cr−CO bond is still longer than the other Cr−C bonds. The activation energy for the transformation **C** → **D1** → **E1** is 106 kJ/mol.

The calculated Gibbs free energy difference between **E1** (+ CO) and **C** is 25 kJ/mol. The ensuing geometry reorganization of **E1** into **G1** proceeds (almost) barrierless; a transition state could not be located. This step is exergonic by 14 kJ/mol. A related dynamic coordination site exchange of the C=C and one CO ligand between the two chromium atoms (windshield wiper mechanism) in [(CO)$_5$Cr(μ−η^1,η^2-C=CR$_2$)Cr(CO)$_4$] (CR$_2$ = CMe$_2$; C(CH$_2$)$_5$; C(Me)Et; C(Me)*t*Bu) has been proposed to account for their NMR spectroscopic features.[27] The energy barrier for dissociation of "Cr(CO)$_4$" from **G1** to afford (CO)$_5$W=C=C=CMe$_2$] (**Ia**) again is very high (Figure 1), rendering this pathway unlikely.

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(28) (a) Froom, S. F. T.; Green, M.; Mercer, R. J.; Nagle, K. R.; Orpen, A. G.; Schwiegk S. *Chem. Commun.* **1986**, 1666, (b) Froom, S. F. T.; Green, M.; Mercer, R. J.; Nagle, K. R.; Orpen, A. G.; Rodriguez, R. A. *J. Chem. Soc., Dalton Trans.* **1991**, 3171.

(29) (a) Capon, J.-F.; Le Berre-Cosquer, N.; Leblanc, B.; Kergoat, R. *J. Organomet. Chem.* **1996**, *508*, 31. (b) Capon, J.-F.; Le Berre-Cosquer, N.; Chuburu, F.; Kergoat, R.; Saillard, J.-Y. *Inorg. Chim. Acta* **1996**, *250*, 119. (c) Capon, J.-F.; Berre-Cosquer, L.; Bernier, S.; Pichon, R.; Kergoat, R.; L'Haridon, P. *J. Organomet. Chem.* **1995**, *487*, 201.

(30) Fischer, H.; Zeuner, S.; Ackermann, K. *Chem. Commun.* **1984**, 684.

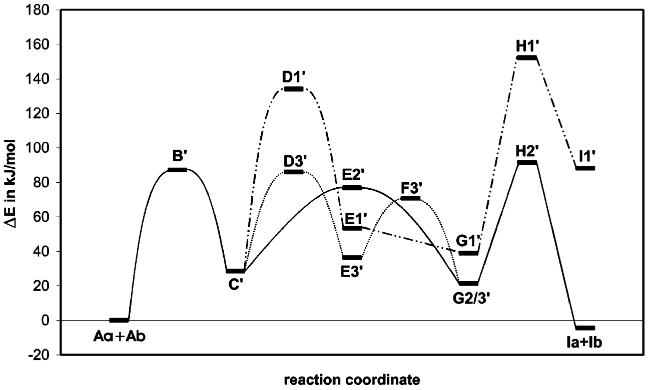
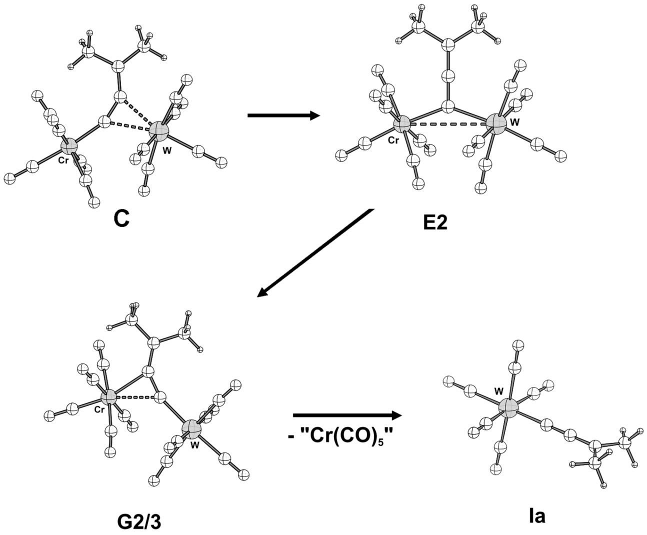


Figure 1. Gibbs free energy profile for the associative pathway of the reaction of $[(CO)_5Cr{=}C{=}C{=}CMe_2]$ with $[(CO)_5W(THF)]$. The energy values for **B′**−**H′** correspond to the structures **B**−**H** shown in eqs 8−11 and include THF; the value of **I1** corresponds to **Ia** + $[(CO)_4Cr(THF)_2]$.

Scheme 10



Pathway 2. An alternative route leads directly, without loss of a CO ligand, via transition state **E2**, to the tungsten allenylidene complex **G2/3**, containing a “$(CO)_5Cr$” fragment coordinated to the $C_\alpha{=}C_\beta$ bond of allenylidene pentacarbonyl tungsten. In **E2** the “$C{=}C{=}CMe_2$” fragment almost “symmetrically” bridges the two metal atoms ($d(Cr-C_\alpha) = 2.15$ Å, $d(W-C_\alpha) = 2.25$ Å), and both methyl groups only slightly deviate from the plane formed by the atoms Cr, W, and C_α (torsional angle $W-C_\alpha-C_\gamma-C(Me)$: 15°). Comparable structures have been found in binuclear molybdenum allenylidene complexes $[\{Cp(CO)_2Mo\}_2C{=}C{=}C(R^1)R^2]$.[28,29] In **G2/3** the torsional angle $W-C_\alpha-C_\gamma-C(Me)$ is 7°. The overall free reaction enthalpy (**C** → **G2/3**) is −7 kJ/mol, and the free energy of activation (**C** → **E2**) is 48 kJ/mol. Dissociation of “$(CO)_5Cr$” from **G2/3** finally affords **Ia**. This process requires an activation energy of 71 kJ/mol. Coordinatively unsaturated “$(CO)_5Cr$” either adds THF to form $(CO)_5Cr(THF)$ (**Ib**) (Scheme 10) or decomposes further to give, among other products, $[Cr(CO)_6]$.

Pathway 3. Another mechanism (Scheme 11) involves intermediate **E3**. **E3** also contains a “symmetrically” bridging allenylidene ligand; however, the (Me)C−C−C(Me) plane and the $W-C_\alpha-Cr$ plane in **E3** are orthogonal. The activation barrier for the transformation **C** → **E3** via **D3** is 57 kJ/mol. **E3** is slightly less stable than **C** ($\Delta G = 8$ kJ/mol). **E3** subsequently rearranges via **F3** into **G2/3** ($\Delta G = -15$ kJ/mol, $\Delta G^\ddagger = 34$ kJ/mol). The next reaction step is identical to that of pathway 2. Pathways 2 and 3 essentially differ in the relative orientation of the (Me)C−C−C(Me) plane during the transformation of **C** into **G2/3**. Whereas in pathway 3 the (Me)C−C−C(Me) and the $Cr-C_\alpha-W$ planes rotate against each other, in pathway 2 both planes remain (almost) coplanar.

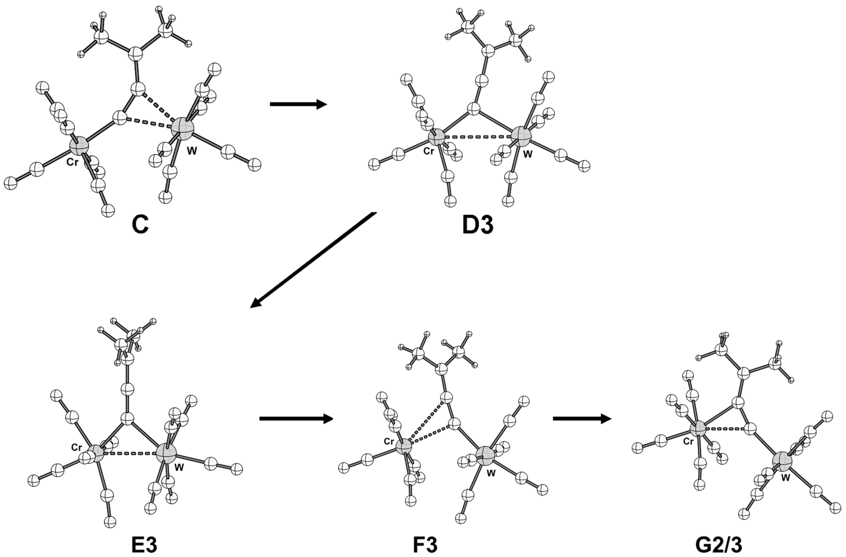
Potential energy profiles for these associative pathways (at 298 K) are depicted in Figure 1.

From a comparison of the free energies it follows that pathway 1 can be excluded. Pathways 2 and 3 have the last step (**G2/3** → **Ia** + **Ib** via **H2/3**) in common. The various transition states along these two differing pathways (**D3**, **E2**, and **F3**) differ only slightly in energy. **H2**, common to both pathways, is higher in energy than **E2** and **D3** by 15 kJ/mol (**E2**) and 6 kJ/mol (**D3**). The two transition states **D3** and **E2** differ only by 9 kJ/mol. Therefore, due to this small difference in energy, both pathways are presumably operative.

Experimental Section

All operations were performed in a dry nitrogen atmosphere using standard Schlenk techniques. Solvents were dried by distillation from CaH_2 (CH_2Cl_2), $LiAlH_4$ (pentane), and sodium (THF). The

Scheme 11



silica gel used for chromatography (Baker, silica for flash chromatography) was nitrogen-saturated. The reported yields refer to analytically pure compounds and are not optimized. Instrumentation: ^{1}H and ^{13}C spectra were recorded at 400 MHz (^{1}H) and 100.5 MHz (^{13}C) at ambient temperature. Chemical shifts are relative to the residual solvent peaks. 2-Ethynyl pyrimidine,[31] methyl(1-phenylpro-2-ynylidene)amine,[32] and the complexes **3a**,**b**,[33] **4a**,**b**, **5a**,**b**, **6a**,**b**, **8a**,**b**,[23] **9a**,**b**,[34] and [M(CO)$_6$][34] were prepared according to literature procedures.

Preparation of Complexes 1 and 2. A solution of 3.1 mL of *n*-BuLi (5 mmol, 1.6 M in *n*-hexane) was added at −80 °C dropwise to a solution of 0.52 g (5 mmol) of 2-ethynylpyrimidine in 50 mL of dry THF. The solution was stirred for 20 min at this temperature. Then 50 mL of a 0.1 M solution of [(CO)$_5$M(THF)] (M = Cr, W) in THF was added. The cooling bath was removed, and the brown solution was stirred for 30 min at ambient temperature. The solvent was removed in vacuo. The remaining oily residue was dissolved in 50 mL of CH$_2$Cl$_2$, treated at 0 °C with 0.95 g (5 mmol) of [Et$_3$O]BF$_4$, and stirred for a further 60 min at this temperature. The resulting deeply colored solution was filtered at −20 °C through a 5 cm layer of silica gel using CH$_2$Cl$_2$ as the eluant. The solvent was removed in vacuo, and the residue was chromatographed at −20 °C on silica gel using mixtures of pentane/CH$_2$Cl$_2$ as eluant. The first violet fraction contained the binuclear complex **2a** or **2b**, the following red one the mononuclear complex **1a** or **1b**.

Pentacarbonyl(*N*-ethyl-3-hydropyrimidine-1,2-propadienylidene)chromium (1a): 0.70 g (43%, based on Cr(CO)$_6$), red oil. IR (THF): ν(CO) 2080 vw, 1931 vs, 1905 m; ν(CCC) 2008 m cm^{-1}. ^{1}H NMR (400 MHz, [d$_6$]-acetone): δ 1.54 (t, $^{3}J_{\mathrm{HH}}$ = 7.0 Hz, 3H, CH$_3$), 4.62 (q, $^{3}J_{\mathrm{HH}}$ = 7.0 Hz, 2H, NCH$_2$), 7.49 (m, 1H, PyrH), 8.85 (m, 1H, PyrH), 8.92 (m, 1H, PyrH). ^{13}C NMR (100 MHz, [d$_6$]-acetone): δ 14.4 (CH$_3$), 54.9 (NCH$_2$), 113.4 (C$_\beta$), 117.1, 151.6, 164.8 (3 PyrC), 137.8 (C$_\gamma$), 188.7 (C$_\alpha$), 219.1 (*cis*-CO), 223.4 (*trans*-CO). MS (FAB): *m*/*z* (%) 324 (38) [M$^+$], 296 (28) [(M − CO)$^+$], 268 (51) [(M − 2CO)$^+$], 240 (33) [(M − 3CO)$^+$], 212 (68) [(M − 4CO)$^+$], 184 (100) [(M − 5CO)$^+$]. UV/vis: $\lambda_{\max}$ (log ϵ) 482 (4.124) [CH$_2$Cl$_2$]. C$_{13}$H$_8$N$_2$O$_5$Cr (324.26).

Pentacarbonyl(*N*-ethyl-3-hydropyrimidine-1,2-propadienylidene)tungsten (1b): 0.82 g (36%, based on W(CO)$_6$), red oil. IR (THF): ν(CO) 2083 vw, 1926 vs, 1900 m; ν(CCC) 2009 m cm^{-1}. ^{1}H NMR (400 MHz, [d$_6$]-acetone): δ 1.55 (t, $^{3}J_{\mathrm{HH}}$ = 7.1 Hz, 3H, CH$_3$), 4.62 (q, $^{3}J_{\mathrm{HH}}$ = 7.0 Hz, 2H, NCH$_2$), 7.57 (dd, $^{3}J_{\mathrm{HH}}$ = 4.7 Hz, $^{3}J_{\mathrm{HH}}$ = 6.3 Hz, 1H, PyrH), 8.91 (m, $^{3}J_{\mathrm{HH}}$ = 6.3 Hz, $^{4}J_{\mathrm{HH}}$ = 2.3 Hz, 1H, PyrH), 8.96 (m, $^{3}J_{\mathrm{HH}}$ = 4.7 Hz, $^{4}J_{\mathrm{HH}}$ = 2.3 Hz, 1H, PyrH). ^{13}C NMR (100 MHz, [d$_6$]-acetone): δ 14.4 (CH$_3$), 55.0 (NCH$_2$), 111.3 (C$_\beta$), 117.6, 151.8, 164.7 (3 PyrC), 142.6 (C$_\gamma$), 170.5 (C$_\alpha$), 198.2 (*cis*-CO, $^{1}J_{\mathrm{WC}}$ = 125.0 Hz), 202.6 (*trans*-CO). MS (FAB): *m*/*z* (%) 456 (42) [M$^+$], 400 (13) [(M − 2CO)$^+$], 372 (33) [(M − 3CO)$^+$], 344 (72) [(M − 4CO)$^+$], 316 (100) [(M − 5CO)$^+$]. UV/vis: $\lambda_{\max}$ (log ϵ) 477 (4.131) [CH$_2$Cl$_2$]. C$_{13}$H$_8$N$_2$O$_5$W (456.11).

Pentacarbonyl(*N*-ethyl-*N*′-pentacarbonylchromium-3-hydropyrimidine-1,2-propadienylidene)chromium (2a): 0.64 g (25%, based on Cr(CO)$_6$), violet oil. IR (THF): ν(CO) 2081 vw, 2068 w, 1943 s, 1929 vs, 1904 sh, 1900 sh; ν(CCC) 1991 m cm^{-1}. ^{1}H NMR (400 MHz, [d$_6$]-acetone): δ 1.63 (t, $^{3}J_{\mathrm{HH}}$ = 7.0 Hz, 3H, CH$_3$), 4.73 (q, $^{3}J_{\mathrm{HH}}$ = 7.0 Hz, 2H, NCH$_2$), 7.47 (m, 1H, PyrH), 9.05 (m, 1H, PyrH), 9.56 (m, 1H, PyrH). ^{13}C NMR (100 MHz, [d$_6$]-acetone): δ 13.9 (CH$_3$), 57.1 (NCH$_2$), 119.2 (C$_\beta$), 114.8, 153.6, 169.8 (3 PyrC), 139.9 (C$_\gamma$), 214.4 (*cis*-CO), 214.6 (C$_\alpha$), 218.1 (*cis*-CO), 220.2 (*trans*-CO), 222.9 (*trans*-CO). MS (FAB): *m*/*z* (%) 516 (6) [M$^+$], 460 (7) [(M − 2CO)$^+$], 432 (8) [(M − 3CO)$^+$], 324 (100) [(M − Cr(CO)$_5$$^+$], 184 (34) [(M − Cr(CO)$_5$ − 5CO$^+$]. UV/vis: $\lambda_{\max}$ (log ϵ) 525 (4.001) [CH$_2$Cl$_2$]. Anal. Calcd for C$_{18}$H$_8$N$_2$O$_{10}$Cr$_2$ (516.26): C, 41.88; H, 1.56; N, 5.43. Found: C, 41.94; H, 1.62; N, 5.56.

Pentacarbonyl(*N*-ethyl-*N*′-pentacarbonyltungsten-3-hydropyrimidine-1,2-propadienylidene)tungsten (2b): 0.66 g (17%, based on W(CO)$_6$), violet oil. IR (THF): ν(CO) 2086 vw, 2072 w, 1940 s, 1922 vs, 1904 sh, 1898 sh; ν(CCC) 1986 m cm^{-1}. ^{1}H NMR (400 MHz, [d$_6$]-acetone): δ 1.65 (t, $^{3}J_{\mathrm{HH}}$ = 7.1 Hz, 3H, CH$_3$), 4.76 (q, $^{3}J_{\mathrm{HH}}$ = 7.2 Hz, 2H, NCH$_2$), 7.54 (t, $^{3}J_{\mathrm{HH}}$ = 5.8 Hz, 1H, PyrH), 9.18 (dd, $^{3}J_{\mathrm{HH}}$ = 5.9 Hz, $^{4}J_{\mathrm{HH}}$ = 2.4 Hz, 1H, PyrH), 9.77 (dd, $^{3}J_{\mathrm{HH}}$ = 5.8 Hz, $^{4}J_{\mathrm{HH}}$ = 2.2 Hz, 1H, PyrH). ^{13}C NMR (100 MHz, [d$_6$]-acetone): δ 13.9 (CH$_3$), 57.5 (NCH$_2$), 117.5 (C$_\beta$), 116.0, 154.1, 170.5 (3 PyrC), 142.1 (C$_\gamma$), 197.4 (*cis*-CO), 198.8 (*cis*-CO), 200.1 (C$_\alpha$), 203.2 (*trans*-CO), 203.9 (*trans*-CO). MS (FAB): *m*/*z* (%) 780 (7) [M$^+$], 724 (63) [(M − 2CO)$^+$], 396 (39) [(M − 3CO)$^+$], 668 (41) [(M − 4CO)$^+$], 640 (42) [(M − 5CO)$^+$], 456 (51) [(M − W(CO)$_5$$^+$], 428 (100) [(M − W(CO)$_5$ − CO$^+$], 316 (40) [(M − W(CO)$_5$ −5CO)$^+$]. UV/vis: $\lambda_{\max}$ (log ϵ) 522 (3.971) [CH$_2$Cl$_2$]. Anal. Calcd for C$_{18}$H$_8$N$_2$O$_{10}$W$_2$ (779.97): C, 27.72; H, 1.03; N, 3.59. Found: C, 27.78; H, 1.19; N, 3.62.

Reaction of 1a with [(CO)$_5$Cr(THF)] or 2b with [(CO)$_5$W(THF)]. [(CO)$_5$Cr(THF)] (10 mL of a 0.1 M solution in THF) {[of [(CO)$_5$W(THF)]: 25 mL of a 0.1 M solution in THF} was added to a solution of 65 mg (0.2 mmol) of **1a** [103 mg (0.2 mmol) of **2a**] in 2 mL of THF. The solution was stirred for 6 h at ambient temperature. The solvent was removed in vacuo and the residue filtered over a short layer of silica using CH$_2$Cl$_2$ as the eluant. The violet band, containing the binuclear complexes **2a** (42 mg; 0.08 mmol; 41%) and **2b** (150 mg; 0.19 mmol; 96%), was collected.

Reactions of 2a or 2b with Et$_3$N, PPh$_3$, or air. A solution of 100 mg (0.2 mmol) of **2a** [1.56 g (0.2 mmol) of **2b**] in 10 mL of CH$_2$Cl$_2$ was treated with 2 mmol of Et$_3$N or PPh$_3$ and stirred for 120 min at ambient temperature. Alternatively, the solutions of the binuclear complexes **2a** and **2b** were exposed to air for the same period of time. The solvent was removed in vacuo and the residue filtered over a short layer of silica using CH$_2$Cl$_2$ as the eluant. The first yellow fraction contained the chromium complexes [(CO)$_5$Cr−L] (L = NEt$_3$,[35] PPh$_3$,[36] CO; characterized by their IR spectra). The following red band contained the mononuclear allenylidene complex **1a** (63 mg; 0.19 mmol; 97%) or **1b** (88 mg; 0.19 mmol; 96%) in almost quantitative yield. When only a small excess of Et$_3$N or PPh$_3$ (1.1 equiv) is used, the reaction proceeds slower and the yields slightly decrease.

Reaction of 1a with [(CO)$_5$W(THF)]. A solution of [(CO)$_5$W(THF)] (30 mL, 0.1 M in THF) was added to 0.32 g (1 mmol) of **1a** in 2 mL of THF. The solution was stirred for 3 h at ambient temperature. The solvent was removed in vacuo and the residue filtered over a short layer of silica using CH$_2$Cl$_2$ as the eluant. The violet band was collected. Removal of the solvent in vacuo yielded 0.61 g (0.78 mmol; 78%) of the dinuclear complex **2b**.

Pentacarbonyl[3-butyl(methyl)amino-3-phenyl-1,2-propadienylidene]chromium (7a). A solution of *n*-BuLi (3.1 mL, 5 mmol, 1.6 M in *n*-nexane) was added at −80 °C dropwise to a solution of 0.52 g (5 mmol) of methyl(1-phenylpro-2-ynylidene)amine in 50 mL of dry THF. The solution was stirred for 20 min at −80 °C. Then 50 mL of a solution of [(CO)$_5$Cr(THF)] (0.1 M in THF) was added. The cooling bath was removed, and the brown solution was stirred for 30 min at ambient temperature. The solvent was removed in vacuo. The remaining oily residue was dissolved in 50 mL of CH$_2$Cl$_2$, treated at 0 °C with 2.22 g (10 mmol) of *n*-BuOTos, and stirred for 16 h at ambient temperature. The resulting deep red solution was filtered through a 5 cm layer of silica gel at −20 °C using CH$_2$Cl$_2$ as the eluant. The solvent was removed in vacuo, and the residue was chromatographed on silica gel at −20 °C using

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[31] Lottermoser, U.; Rademacher, P.; Mazik, M.; Kowski, K. *Eur. J. Org. Chem.* **2005**, 522.

[32] Schlegel, J.; Maas, G. *Synthesis* **1999**, 100.

[33] Roth, G.; Fischer, H. *Organometallics* **1996**, *15*, 1139.

[34] Fischer, H.; Reindl, D.; Roth, G. *Z. Naturforsch.* **1994**, *49b*, 1207.

[35] Strohmeier, W.; Guttenberger, J. F.; Blumenthal, H.; Albert, G. *Chem. Ber*. **1966**, *99*, 3419.

[36] Chalmers, A. A.; Lewis, J.; Whyman, R. *J. Chem. Soc., Sect. A* **1967**, *11*, 1817.

a mixture of pentane/CH_2Cl_2 (2:1) as eluant, yielding 1.02 g (52%) of **7a** as a red-brown oil. The ^{1}H NMR spectrum in d_6-acetone (integration of the NCH_3 signals) revealed a 5:2 mixture of the inseparable *E*- and *Z*-isomers. IR (THF): ν(CO) 1929 vs, 1905 m; ν(CCC) 1994 m cm^{-1}. ^{1}H NMR (400 MHz, [d_6]-acetone) (*E*)-**7a**: δ 1.04 (t, $^3J_{HH}$ = 7.4 Hz, 3H, NBu), 1.55 (m, $^3J_{HH}$ = 7.4 Hz, 2H, NBu), 1.96 (m, $^3J_{HH}$ = 7.4 Hz, 2H, NBu), 3.43 (s, 3H, NCH_3), 4.17 (t, $^3J_{HH}$ = 7.4 Hz, 2H, NBu), 7.52 (m, 3H, ArH), 7.62 (m, 2H, ArH); (*Z*)-7a: δ 0.81 (t, $^3J_{HH}$ = 7.4 Hz, 3H, NBu), 1.20 (m, $^3J_{HH}$ = 7.4 Hz, 2H, NBu), 1.75 (m, $^3J_{HH}$ = 7.4 Hz, 2H, NBu), 3.72 (t, $^3J_{HH}$ = 7.4 Hz, 2H, NBu), 3.76 (s, 3H, NCH_3), 7.52 (m, 3H, ArH), 7.62 (m, 2H, ArH). ^{13}C NMR (100 MHz, [d_6]-acetone) (*E*)-**7a**: δ 14.0, 20.5, 30.3, 41.4 (4 NBu), 58.1 (NCH_3), 121.8 (C_β), 129.2, 129.4, 132.0, 135.5 (4 ArC), 154.9 (C_γ), 217.6 (C_α), 218.6 (*cis*-CO), 224.2 (*trans*-CO); **(***Z***)**-7a. δ 13.6, 20.1, 29.3, 42.4 (4 NBu), 55.1 (NCH_3), 123.1 (C_β), 128.5, 129.5, 131.6, 135,6 (4 ArC), 155.6 (C_γ), 218.6 (*cis*-CO), 221.3 (C_α), 224.3 (*trans*-CO). MS (EI): *m*/*z* (%) 391 (27) [M^+], 307 (9) [$(M - 3CO)^+$], 279 (35) [$(M - 4CO)^+$], 251 (100) [$(M - 5CO)^+$]. UV/vis: λ_{max} (log ϵ) 477 (4.288) [CH_2Cl_2]. Anal. Calcd for $C_{19}H_{17}CrNO_5$ (391.34): C, 58.31; H, 4.38; N, 3.58. Found: C, 58.29; H, 4.51; N, 3.61.

General Procedure for the Transmetalation. A solution of 0.5 mmol of the appropriate chromium allenylidene complexes (**3a**−**9a**) was treated with 15 mL of a solution of [$(CO)_5W(THF)$] (0.1 M) in THF and stirred for 6 h at ambient temperature. The solvent was removed in vacuo and the residue filtered over a short layer of silica using mixtures of pentane/CH_2Cl_2 as the eluant. The strongly colored bands were collected and the solvent was removed in vacuo, yielding the product complexes **3b**−**9b**, which were identified by their known spectroscopic data (except for **7b**; see below). Yields: 206 mg (0.46 mmol; 92%) of **3b**; 210 mg (0.48 mmol; 97%) of **4b**; 230 mg (0.48 mmol; 96%) of **5b**; 213 mg (0.43 mmol; 86%) of **6b**; 240 mg (0.46 mmol; 92%) of **7b**; 260 mg (0.46 mmol; 93%) of **8b**; 250 mg (0.41 mmol; 83%) of **9b**.

Pentacarbonyl[3-butyl(methyl)amino-3-phenyl-1,2-propadienylidene]tungsten (7b): redish-brown oil. The ^{1}H NMR spectrum in d_6-acetone (integration of the NCH_3 signals) revealed a 5:2 mixture of the inseparable *E*- and *Z*-isomers. IR (THF): ν(CO) 1930 vs, 1905 m; ν(CCC) 1994 m cm^{-1}. ^{1}H NMR (400 MHz, [d_6]-acetone) (*E*)-**7b**: δ 0.91 (t, $^3J_{HH}$ = 7.4 Hz, 3H, NBu), 1.43 (m, $^3J_{HH}$ = 7.4 Hz, 2H, NBu), 1.90 (m, $^3J_{HH}$ = 7.4 Hz, 2H, NBu), 3.33 (s, 3H, NMe), 4.05 (t, $^3J_{HH}$ = 7.4 Hz, 2H, NBu), 7.40−7.70 (m, 5H, ArH); (*Z*)-**7b**: δ 0.69 (t, $^3J_{HH}$ = 7.4 Hz, 3H, NBu), 1.08 (m, $^3J_{HH}$ = 7.4 Hz, 2H, NBu), 1.69 (m, $^3J_{HH}$ = 7.4 Hz, 2H, NBu), 3.59 (t, $^3J_{HH}$ = 7.4 Hz, 2H, NBu), 3.64 (s, 3H, NMe), 7.40−7.70 (m, 5H, ArH). ^{13}C NMR (100 MHz, [d_6]-acetone) (*E*)-**7b**: δ 13.9, 20.5, 30.1, 41.6 (4 NBu), 58.4 (NMe), 119.3 (C_β, $^2J_{WC}$ = 25.0 Hz), 129.1, 129.4, 132.1, 135,4 (4 ArC), 156.7 (C_γ), 194.5 (C_α, $^1J_{WC}$ = 101.9 Hz), 197.8 (*cis*-CO, $^1J_{WC}$ = 124.0 Hz), 203.7 (*trans*-CO, $^1J_{WC}$ = 130.8 Hz); (*Z*)-**7b**: δ 13.6, 20.1, 29.3, 42.7 (4 NBu), 55.3 (NMe), 120.6 (C_β), 128.4, 129.6, 131.7, 135.5 (4 ArC), 157.4 (C_γ), 197.7 (C_α), 197.8 (*cis*-CO), 203.8 (*trans*-CO). MS (EI): *m*/*z* (%) 523 (24) [M^+], 495 (28) [$(M - CO)^+$], 467 (32) [$(M - 2CO)^+$], 409 (21) [$(M - 4CO)^+$], 383 (70) [$(M - 5CO)^+$]. UV/vis: λ_{max} (log ϵ) 465 (4.367) [CH_2Cl_2]. Anal. Calcd for $C_{19}H_{17}NO_5W$ (523.20): C, 43.62; H, 3.28; N, 2.68. Found: C, 43.86; H, 3.46; N, 2.87.

Computational Details. All ab initio calculations were performed using Jaguar[37] (version 5.5.016) running on Linux- 2.4.20-28.7smp on six Athlon MP 2400+ dual-processor workstations (Beowulf cluster) parallelized with MPICH 1.2.4. Initial structures were obtained by MM+ optimization using Hyperchem.[38] Geometries were optimized using the LACVP* basis set (ECP for Cr and W, N31G6* for all other atoms) and the BP86 density functional. Calculation of the second derivatives at 298.15 K ensured that true minima were found by showing no large negative frequencies. All reported energies are Gibbs free energies at 298 K.

Transition states of reorganization reactions were obtained by using the QST (quadratic synchronous transit) method implemented in Jaguar, using an interpolated structure between starting compound and product as a transition state guess. After calculating the second derivative at 298.15 K, all transition states showed exactly one imaginary frequency in the direction of the reaction coordinate. Additionally, IRC (intrinsic reaction coordinate) calculations were performed in both directions, leading to product and starting compound. All reported activation energies are Gibbs free activation energies at 298 K. To access the transition states of CO dissociations and $(CO)_5W$ associations, geometry scans involving the stepwise increase or decrease of the corresponding bonding distance have been used, including geometry optimization of all other degrees of freedom for each step. The maximum energy structures from these geometry scans were used as transition state guesses for a standard (simple quasi-Newton) transition state search implemented in Jaguar. Again, second derivatives were used for transition state validation.

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Supporting Information Available: Text giving the Cartesian coordinates and energies (at 298 K) of the starting compounds, the product complexes, the optimized minima, the transition states, and the fragments. This material is available free of charge via the Internet at http://pubs.acs.org.

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[37] *Jaguar 5.5*; Schrödinger, LLC: Portland, OR, 2003.

[38] *Hyperchem* (version 5); Hypercube Inc.: Gainsville, FL 32601.