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Alkynylcarbyne(bipyridine)dicarbonyl(triflouroacetato) complexes—synthesis and detection of reversible association in solution

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Abstract

A series of alkynylcarbyne(bipyridine)(dicarbonyl)trifluoroacetato complexes, [$CF_3COO(L{-}L)(CO)_2M{\equiv}C{-}C{\equiv}C{-}R$] (M = W, Mo; L–L = 2,2′-bipyridine, 4,4′-dimethyl 2,2′-bipyridine; R = $SiMe_3$, Ph, *p*-Tol, *t*-Bu), has been prepared by sequential reaction of [$M(CO)_6$] with Li[C≡CR], trifluoroacetic anhydride, and L–L. All complexes were fully characterized. Concentrated solutions of these complexes exhibit two sets of $\nu(CO)$ absorptions (instead of the expected one set (A_1/B_1). The ratio $A_1/B_1{:}A_1^*/B_1^*$ is concentration-dependent and decreases with increasing concentration of the complexes in solution. This phenomenon is discussed on the basis of a reversible association of complex molecules to form dimers and oligomers prior to precipitation and crystallization.

Keywords: Carbyne complexes; Infrared spectra; Concentration-dependence; Tungsten; Molybdenum

1. Introduction

The synthesis of the first transition metal carbyne complexes (alkylidyne complexes) was reported by Fischer et al. in 1973 [1], that of the first transition metal alkynylcarbyne(tetracarbonyl) complexes (alkynylidyne complexes), $X(CO)_4W{\equiv}C{-}C{\equiv}C{-}Ph$ (X = Cl, Br, I), already 1 year later [2]. Ten years later, *t*-butylethynylcarbyne(dicarbonyl) complexes containing bi- and tridentate ligands, $L_3(CO)_2M{\equiv}C{\equiv}C{-}(t\text{-Bu})$ (M = Mo, W), were described by Stone et al. [3]. The reactivity and the electronic properties of these alkynylcarbyne complexes were only marginally explored. Recently, we reported on the synthesis of several trimethylsilyl- and phenylethynylcarbyne complexes and on the influence of various electron-donating tripodal co-ligands on the spectroscopic properties of the new compounds [4]. When we extended our studies to alkynylcarbyne complexes with bidentate N-donor co-ligands an unusual dependence of the IR spectra of the complexes on the concentration was observed.

2. Results and discussion

The new alkynylcarbyne dicarbonyl complexes containing bipyridine or 4,4′-dimethyl-2,2′-bipyridine and trifluoroacetate as co-ligands were prepared by the reaction sequence shown in the Scheme 1. Addition of Li[C≡C–R] to [$M(CO)_6$] in THF or Et_2O gave acyl metallates. Subsequent oxide abstraction with trifluoroacetic anhydride at −80 °C [5] afforded *trans*-alkynylcarbyne(tetracarbonyl)trifluoroacetato complexes which were transformed into the alkynylcarbyne(dicarbonyl) complexes **1a**,**b**–**7a**,**b** by addition of bipyridine and 4,4′-dimethyl-2,2′-bipyridine, respectively.

The new compounds **1a**,**b**–**7a**,**b** are more stable than those alkynylcarbyne(tetracarbonyl) complexes of tungsten previously mentioned and are even more stable

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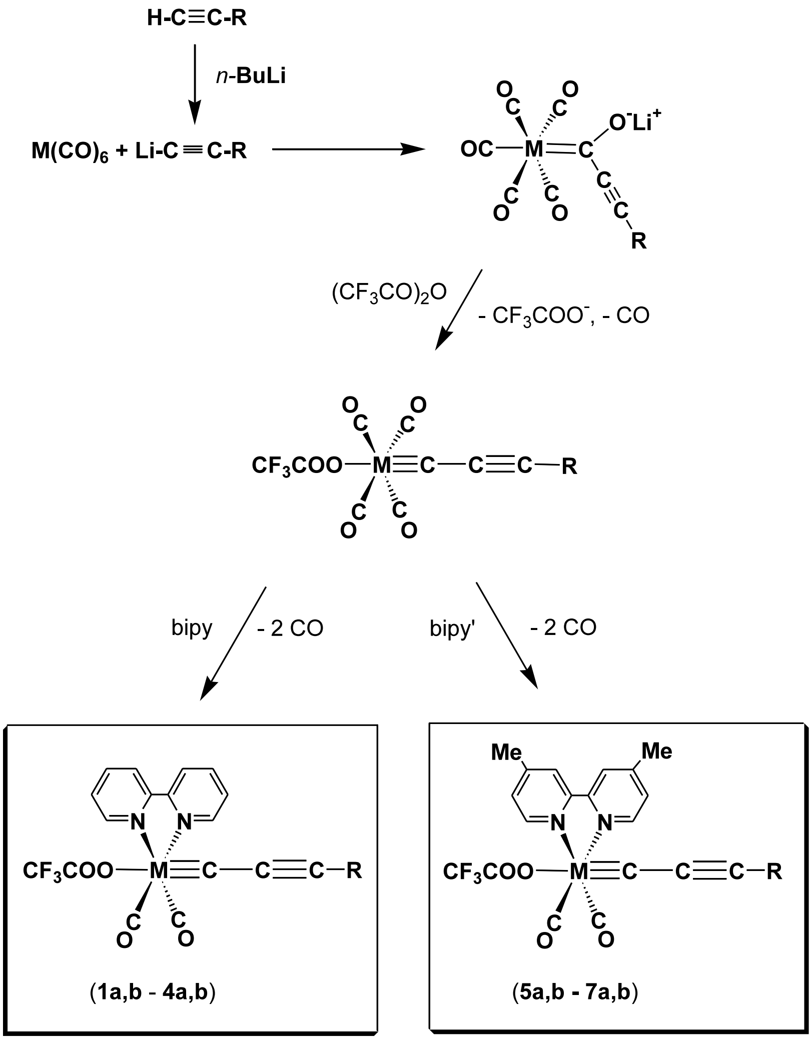


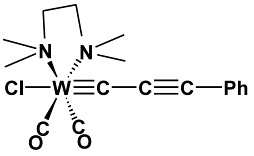
M = W (**a**), Mo (**b**)

R = $SiMe_3$ (**1, 5**), Ph (**2, 6**), *p*-Tol (**3, 7**), *t*-Bu (**4**)

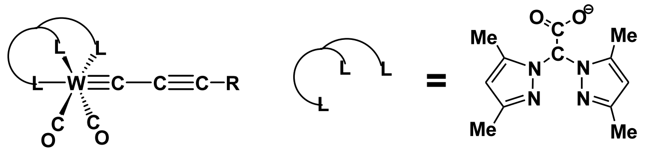
Scheme 1.

than the complexes $[L_3(CO)_2W{\equiv}C{-}C{\equiv}C{-}R]$ ($L_3 =$ Tp, Tp′, Cp; R = $SiMe_3$, Ph, *n*-Bu) [3,4]. At −30 °C, **1a**,**b**–**7a**,**b** can be stored under an inert gas atmosphere for prolonged periods of time without noticeable decomposition but they decompose in solution at room temperature within about 2–3 days. The complex **1a**,**b**–**7a**,**b** are insoluble in nonpolar solvents and only moderately soluble in polar solvents.

The IR spectra of the complexes **1a**,**b**–**7a**,**b** in tetrahydrofuran exhibit an unusual behavior: the ν(CO) absorptions are concentration-dependent. The pattern of two ν(CO) absorptions of nearly equal intensity (A_1 and B_1) as expected for *cis*-dicarbonyl transition metal complexes is observed only with very diluted solutions (in most cases concentration < 0.01 mol l^{-1}). When the concentration of the complexes is increased two additional ν(CO) absorptions appear at lower wave numbers (A_1^* and B_1^*). With increasing concentration of **1a**,**b**–**7a**,**b** the relative intensity of A_1^* and B_1^* ν(CO) absorptions increases and that of A_1 and B_1 bands simultaneously decreases. Conversely, diluting concentrated solutions of **1a**,**b**–**7a**,**b** leads to a decrease of the relative intensity of A_1^* and B_1^* and simultaneously to an increase of the intensity of A_1 and B_1 ν(CO) absorptions until finally only the A_1 and B_1 absorptions are detectable. Similar effect are observed when solutions of the *trans*-chloro(dicarbonyl)(TMEDA)phenylethynylcarbyne complex (**8a**) [4] in diethyl ether or of the bdmpza(dicarbonyl)phenylethynylcarbyne complexes **9a** in diethyl ether and **10a** [4] in THF are concentrated or diluted. In all cases the additional bands are found at lower wave numbers.



(**8a**)



R = SiMe$_3$ (**9a**)
Ph (**10a**)

The change of the ν(CO) absorptions when varying the concentration is shown in Fig. 1 with the example of [(CF$_3$CO$_2$)(bipy)(CO)$_2$Mo≡C–C≡C–Ph] (**2b**).

In Fig. 2 these spectra are normalized to the same amount of absorbing molecules. Two isosbestic points, one at 2007 cm^{-1} and one at 1927 cm^{-1}, are observed. Obviously, the formation of a new species as indicated by the additional bands is reversible and concentration-dependent.

The positions of the additional bands A_1^* and B_1^* of **1a**,**b**–**7a**,**b**, **8a**, **9a** and **10a** in general agree well with those of the ν(CO) absorptions in the solid state (KBr pellets). All data are compiled in the Table 1.

The difference in the position of the A_1 positions ($\Delta A_1 = A_1 - A_1^*$) is significantly smaller than that in the B_1 positions ($\Delta B_1 = B_1 - B_1^*$). In general both, ΔA_1 and ΔB_1, are within error limits independent of the metal and of the substituent R, however, depend on the co-ligand. All dimethyl bipyridine substituted complexes (**5a**,**b**–**7a**,**b**) exhibit smaller ΔA_1 and ΔB_1 values than the corresponding bipyridine substituted complexes **1a**,**b**–**3a**,**b**.

The second set of ν(CO) absorptions is only observed when relatively high concentrations (with respect to the solubility) are employed and when the IR spectra are measured in solvents in which the complexes exhibit only poor solubility. For example, solutions of the complexes **8a** and **9a** in diethyl ether show four ν(CO) bands but only two in THF.

These observations indicate that the second set of ν(CO) absorptions is due to a reversible association of complex molecules before nucleation and subsequent precipitation. In concentrated solutions the molecules presumably associate in a way similar to that observed in the solid state. In accord with such an assumption solutions exhibiting strong ν(CO) A_1^* and B_1^* absorptions also show light-scattering effects. From the position of the A_1^* and B_1^* bands at lower wave numbers it follows that the metal of the dimers are more electron-rich than that of the monomers very likely caused by intermolecular interaction of alkynylcarbyne ligands. In concentrated solution, dimers or oligomers of **1a**,**b**–**7a**,**b** and **8a**–**10a** are probably in equilibrium with their monomers.

The structures of **8a** and **10a** have previously been established by X-ray structural analyses [4,6]. Complex **8a** crystallizes with one equivalent of dichloromethane. In the crystal of **8a** dimeric units with a parallel head to tail arrangement of the phenylethynylcarbyne fragments

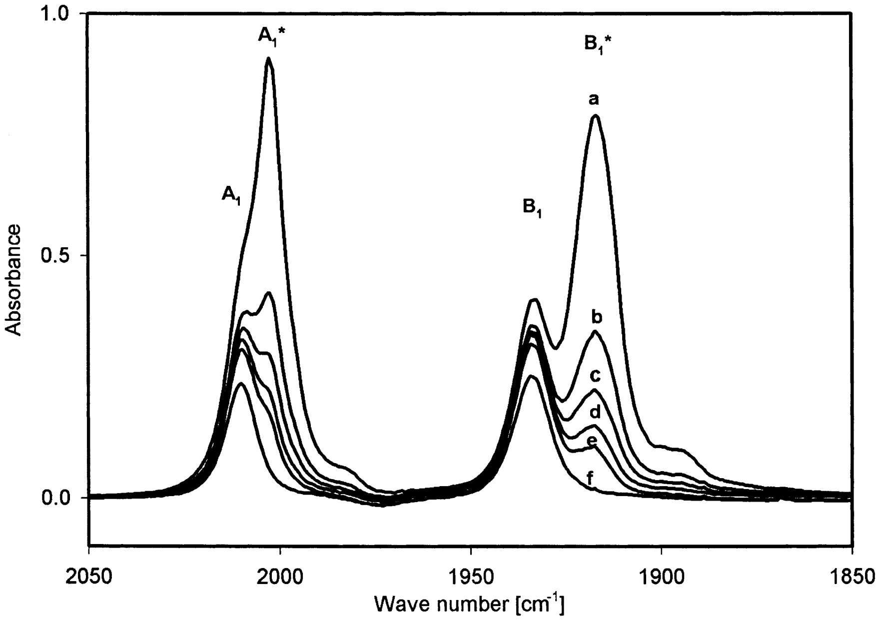


Fig. 1. IR spectra of various concentrations of **2b** in THF [$c = 0.067$ mol l^{-1} (a), 0.042 mol l^{-1} (b), 0.037 mol l^{-1} (c), 0.03 mol l^{-1} (d), 0.028 mol l^{-1} (e), 0.020 mol l^{-1} (f)].

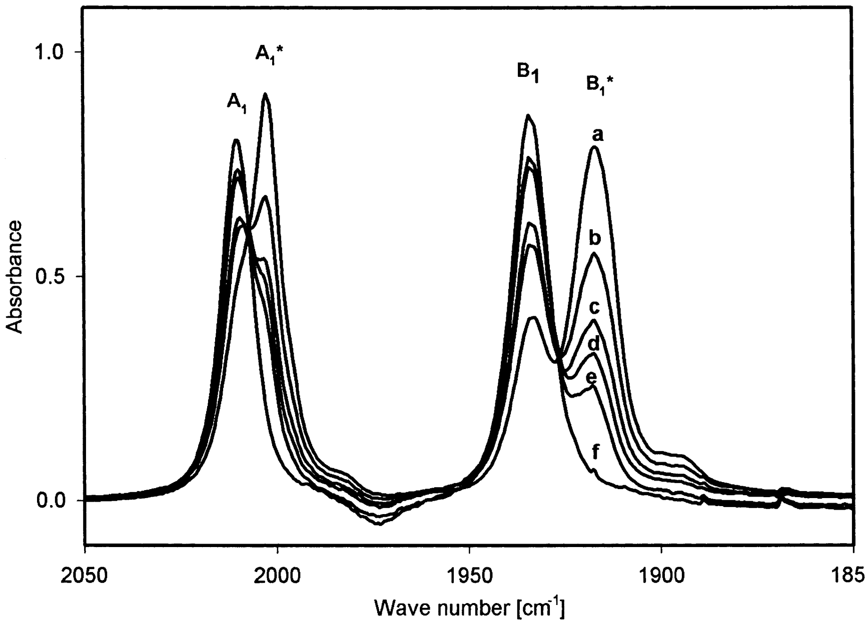


Fig. 2. IR spectra of various concentrations of **2b** in THF normalized to the same amount of **2b** [$c = 0.067$ mol l^{-1} (a), 0.042 mol l^{-1} (b), 0.037 mol l^{-1} (c), 0.03 mol l^{-1} (d), 0.028 mol l^{-1} (e), 0.020 mol l^{-1} (f)].

Table 1
ν(CO) absorptions of the complexes **1**–**10** (in cm^{-1}) in solution (**1**–**7** and **10a** in THF, **8a** and **9a** in Et_2O), and in KBr pellets

	In solution				KBr pellet	
	A_1	B_1	A_1^*	B_1^*	A_1	B_1
1a	2000	1918	1998	1901	1999	1904
1b	2014	1937	2010	1922	2014	1925
2a	1997	1915	1990	1895	1991	1895
2b	2010	1934	2002	1917	2004	1917
3a	1995	1914	1989	1894	1989	1894
3b	2009	1933	2001	1913	2003	1915
4a	1993	1910	1992	1893	1993	1893
5a	1998	1916	1998	1904	2000	1904
5b	2013	1935	2012	1925	2014	1925
6a	1995	1913	1995	1915	1992	1902
6b	2009	1932	2010	1939	2010	1928
7a	1994	1912			1990	1908
7b	2007	1931			2006	1926
8a	1993	1909	1981	1871	1985	1895
9a	1995	1912	1982	1893	1989	1903
10a	1992	1910	1983	1905	1982	1906

are present (Fig. 3). The 'dimers' are separated by dichloromethane molecules. Very likely in concentrated solution similar dimers are reversibly formed giving rise to the shift in the ν(CO) absorptions. The extent of the electronic interaction of both molecules is among other factors determined by the distance within the 'dimers' thus readily explaining the smaller ΔA_1 and ΔB_1 values of dimethyl bipyridine substituted complexes compared with those of the bipyridine substituted complexes.

Complex **10a** crystallizes with one equivalent of THF. Again the alkynylcarbyne fragments arrange in a parallel head-to-tail fashion. However, the separation of the 'dimers' is less pronounced than in **8a**.

These crystal structures support the assumption that dimeric units (and at higher concentration presumably oligomeric units) are the source of the second set of ν(CO) absorptions. Assuming formation of dimers, equilibrium constants ($K = [\text{dimer}]/[\text{monomer}]^2$) for some complexes could be estimated from the IR spectra: $K = 27$ (**2a**), 10 (**2b**), 28 (**3a**), and 36 (**10a**), all values determined at 0.020 mol l^{-1} 'total' concentration of complexes.

Recently the pressure tuning of IR and Raman spectra of some dicarbonyl carbyne complexes of the type $[\{Cl(CO)_2(L{-}L)W{\equiv}CC_6H_4{-}(C{\equiv}CC_6H_4)_n{-}N{\equiv}C\}_2M]$ ($M = PdI_2$ or $ReCl(CO)_3$, L–L = TMEDA, DPPE) was reported by Xu et al. [7] and a pressure induced phase-transition in the solid state of these compounds was observed. In the solid state the $Cl(CO)_2(TMEDA)W$ group of the complex $[\{Cl(CO)_2(TMEDA)W{\equiv}CC_6H_4N{\equiv}C\}_2Re(CO)_3]$ was found to exhibit four instead of the expected two ν(CO) absorptions [7]. The appearance of multiple absorptions was ascribed to the solid-state packing of the molecules. However, to the best of our knowledge the formation of dimers (and oligomers) in solution when increasing the concentration and approaching saturation concentration has not been observed before in carbene and carbyne complex chemistry. Obviously, this association is the first step in the formation of crystals and in precipitation. The detection of associa-

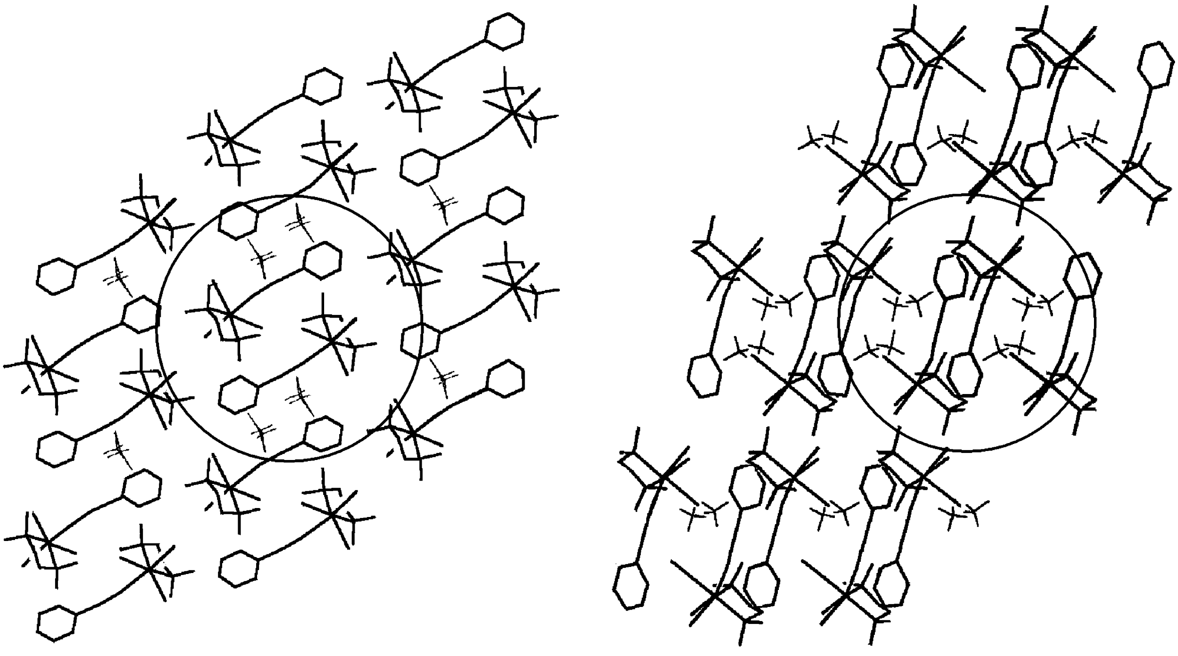


Fig. 3. View along the crystallographic *a* (left) and *b* axis (right) of the crystal structure of complex **8a**. The hydrogen atoms of **8a** are omitted for clarity. The 'dimeric units' separated by dichloromethane molecules from neighboring units are highlighted by a circle each.

tion was facilitated by the rather poor solubility of the complexes **1**–**10**. Other carbyne complexes such as arylcarbyne complexes may exhibit similar effects, however, the usually high solubility of these complexes renders the detection of a similar association difficult. Good candidates for a detection are those complexes that incorporate solvent molecules into the solid state structure [8–10].

3. Experimental

3.1. General

All operations were carried out under either nitrogen or argon by using conventional Schlenk techniques. Solvents were dried by refluxing over sodium-benzophenone ketyl or CaH_2 and were freshly distilled prior to use. The silica gel used for chromatography (J.T. Baker, silica gel for flash chromatography) was saturated with argon. The yields refer to analytically pure compounds and were not optimized. [Cl(tmeda)-$(CO)_2W{\equiv}C{-}C{\equiv}C{-}Ph$], [(bdmpza)$(CO)_2W{\equiv}C{-}C{\equiv}C{-}Ph$] and [(bdmpza)$(CO)_2W{\equiv}C{-}C{\equiv}C{-}SiMe_3$] were prepared as described previously [4]. Trimethylsilylacetylene, *p*-tolylacetylene, 2,2′-bipyridine (Fluka), phenylacetylene (Merck), *n*-*b*utyllithium (Chemetall), tungsten hexacarbonyl, trifluoroacetic anhydride, *t*-butylacetylene, and 4,4′-dimethyl-2,2′-bipyridine (Aldrich) were commercial products and were used without further purification. IR: FTIR spectrophotometer, Bio-Rad. ^{1}H-NMR, ^{13}C-NMR: Bruker AC 250, Bruker DRX 600. Unless specifically mentioned, NMR spectra were recorded at room temperature (r.t.) at 250 MHz (^{1}H) and 151 MHz (^{13}C). Chemical shifts are reported in ppm relative to the residual solvent peaks [CD_3COCD_3: $\delta = 2.04$ (^{1}H) and $\delta = 29.8$ (^{13}C), $CDCl_3$: $\delta = 7.24$ (^{1}H) and $\delta = 79.0$ (^{13}C)]. MS: Finnigan MAT 312 (EI) or Finnigan MAT 312/AMD5000 (FAB).

3.2. General procedure for the synthesis of the complexes (*1a*,*b*–*7a*,*b*)

At −30 °C, 5.0 mmol of the respective acetylene derivative (trimethylsilylacetylene, phenylacetylene, *p*-tolylacetylene and *t*-butylacetylene) in 30 ml of Et_2O was lithiated with *n*-BuLi (15% solution in hexane). After 0.5 h, 5.0 mmol of [$M(CO)_6$] (M = W, Mo) and 5 ml of THF were added. The resulting suspension immediately turned orange. When it was stirred for 1 h at r.t. a clear orange solution was formed. The solution was cooled to −80 °C and 5.0 mmol of $(CF_3CO)_2O$ was added. Evolution of CO was observed. At −50 °C, 5.0 mmol of 2,2′-bipyridine or 4,4′-dimethyl-2,2′-bipyridine, respectively, was added. Then solution was slowly warmed to r.t. CO evolution gradually ceased and a red precipitate was formed. To complete precipitation, pentane was added to the dark red solution. The precipitate was decanted and [$M(CO)_6$] and [$M(bipy)(CO)_4$] (M = W, Mo) were removed from the crude product by repeatedly washing with pentane and pentane–CH_2Cl_2 (3:1). The resulting orange to red product was then dried in vacuo.

*3.2.1. 2,2′-Bipyridyl(dicarbonyl)(trifluoroacetato)-(trimethylsilylpropynylidyne)tungsten (**1a**)*

Yield: 2.19 g (71% relative to $[W(CO)_6]$). Dec. >194 °C. IR (THF, cm^{-1}): ν(C≡C) 2057 vw, ν(CO) 2000 s, 1918 s, ν(C=O) 1689 m. ^{1}H-NMR ($CD_3C(O)CD_3$): $\delta = 0.08$ (s, 9H, $SiMe_3$), 7.89 (t, $^3J = 5.1$ Hz, 2H, C4-H), 8.45 (dt, $^3J = 6.6$ Hz, $^4J = 0.6$ Hz, 2H, C5-H), 8.78 (d, $^3J = 3.4$ Hz, 2H, C3-H), 9.35 (d, $^3J = 2.1$ Hz, 2H, C6-H). ^{13}C-NMR ($CD_3C(O)CD_3$): $\delta = -0.4$ ($SiMe_3$), 76.6 (C_β), 120.7 (C_α), 124.6 (C3, bipy), 128.4 (C5, bipy), 142.2 (C4, bipy), 155.8 (C6, bipy), 156.3 (C2, bipy), 160.6 (q, CF_3CO_2), 225.0 ($^1J(WC) = 171$ Hz, CO), 246.3 (W≡C). MS (EI): m/z (%) = 590 (0.4) $[M^+ - CO]$, 562 (1) $[M^+ - 2CO]$, 505 (0.4) $[M^+ - CF_3CO_2]$, 156 (100) $[C_{10}H_8N_2]$. Anal. Found: C, 38.33; H, 2.94; N, 4.17. Calc. for $C_{20}H_{17}F_3N_2O_4SiW$ (618.3): C, 38.85; H, 2.77; N, 4.53%.

*3.2.2. 2,2′-Bipyridyl(dicarbonyl)(trifluoroacetato)-(trimethylsilylpropynylidyne)molybdenum (**1b**)*

Yield: 2.02 g (64% relative to $[Mo(CO)_6]$). Dec. >156 °C. IR (THF, cm^{-1}): ν(C≡C) 2050 w, ν(CO) 2014 s, 1937 s, ν(C=O) 1685 m. ^{1}H-NMR ($CD_3C(O)CD_3$): $\delta = 0.09$ (s, 9H, $SiMe_3$), 7.82 (dt, $^3J = 6.5$ Hz, $^4J = 1.2$ Hz, 2H, C4-H), 8.38 (dt, $^3J = 7.5$ Hz, $^4J = 1.6$ Hz, 2H, C5-H), 8.70 (dd, $^3J = 8.2$ Hz, $^4J = 0.9$ Hz, 2H, C3-H), 9.21 (dd, $^3J = 4.5$ Hz, $^4J = 0.8$ Hz, 2H, C6-H). ^{13}C-NMR ($CD_3C(O)CD_3$): $\delta = -0.4$ ($SiMe_3$), 72.4 (C_β), 113.7 (C_α), 124.2 (C3, bipy), 127.5 (C5, bipy), 141.8 (C4, bipy), 155.3 (C6, bipy), 155.5 (C2, bipy), 160.8 (q, CF_3CO_2), 226.1 (CO), 253.5 (Mo≡C). MS (FAB, THF/NBA): m/z (%) = 476 (7) $[M^+ - 2CO]$, 419 (11) $[M^+ - CF_3CO_2]$, 363 (9) $[M^+ - CF_3CO_2 - 2CO]$. Anal. Found: C, 45.31; H, 3.49; N, 5.16. Calc. for $C_{20}H_{17}F_3N_2MoO_4Si$ (530.4): C, 45.29; H, 3.23; N, 5.28%.

*3.2.3. 2,2′-Bipyridyl(dicarbonyl)(trifluoroacetato)-(phenylpropynylidyne)tungsten (**2a**)*

Yield: 1.90 g (61% relative to $[W(CO)_6]$). Dec. >183 °C. IR (THF, cm^{-1}): ν(C≡C) 2102 w, ν(CO) 1997 s, 1915 s, ν(C=O) 1688 m. ^{1}H-NMR ($CD_3C(O)CD_3$): $\delta = 7.30$–7.45 (m, 5H, Ph), 7.90 (dt, $^3J = 4.9$ Hz, $^4J = 1.0$ Hz, 2H, C3-H), 8.49 (dt, $^3J = 6.2$ Hz, $^4J = 1.6$ Hz, 2H, C5-H), 8.80 (d, $^3J = 8.0$ Hz, 2H, C4-H), 9.38 (d, $^3J = 5.5$ Hz, 2H, C6-H). ^{13}C-NMR ($CD_3C(O)CD_3$): $\delta = 68.5$ (C_β), 107.1 (C1, Ph), 122.1 (C_α), 124.6 (C3, bipy), 128.3 (C5, bipy), 129.5, 129.8, 133.2 (Ph), 142.1 (C4, bipy), 155.8 (C6, bipy), 156.3 (C2, bipy), 160.8 (q, CF_3CO_2), 225.2 ($^1J(WC) = 170$ Hz, CO), 244.1 (W≡C). MS (FAB, THF/NBA): m/z (%) = 509 (1) $[M^+ - CF_3CO_2]$, 453 (1) $[M^+ - CF_3CO_2 - 2CO]$, 154 (100) $[C_{10}H_8N_2 - 2]$. Anal. Found: C, 43.92; H, 2.25; N, 4.36. Calc. for $C_{23}H_{13}F_3N_2O_4W$ (622.2): C, 44.40; H, 2.11; N, 4.50%.

*3.2.4. 2,2′-Bipyridyl(dicarbonyl)(trifluoroacetato)-(phenylpropynylidyne)molybdenum (**2b**)*

Yield: 1.66 g (62% relative to $[Mo(CO)_6]$). Dec. >180 °C. IR (THF, cm^{-1}): ν(C≡C) 2097 w, ν(CO) 2010 s, 1934 s, ν(C=O) 1684 m. ^{1}H-NMR ($CD_3C(O)CD_3$): $\delta = 7.25$–7.50 (m, 5H, Ph), 7.82 (dt, $^3J = 6.4$ Hz, $^4J = 1.1$ Hz, 2H, C3-H), 8.39 (dt, $^3J = 6.5$ Hz, $^4J = 1.4$ Hz, 2H, C5-H), 8.72 (d, $^3J = 8.1$ Hz, 2H, C4-H), 9.25 (d, $^3J = 4.1$ Hz, 2H, C6-H). ^{13}C-NMR ($CD_3C(O)CD_3$): $\delta = 64.3$ (C_β), 100.7 (C1, Ph), 121.2 (C_α), 124.1 (C3, bipy), 127.5 (C5, bipy), 129.6, 130.4, 133.8 (Ph), 141.8 (C4, bipy), 155.3 (C6, bipy), 155.6 (C2, bipy), 160.4 (q, CF_3CO_2), 226.4 (CO), 251.8 (Mo≡C). MS (FAB, THF/NBA): m/z (%) = 480 (0.5) $[M^+ - 2CO]$, 423 (0.7) $[M^+ - CF_3CO_2]$, 367 (0.7) $[M^+ - CF_3CO_2 - 2CO]$, 154 (100) $[C_{10}H_8N_2 - 2]$. Anal. Found: C, 51.31; H, 2.58; N, 5.07. Calc. for $C_{23}H_{13}F_3MoN_2O_4$ (534.3): C, 51.70; H, 2.45; N, 5.24%.

*3.2.5. 2,2′-Bipyridyl(dicarbonyl)(trifluoroacetato)-(p-tolylpropynylidyne)tungsten (**3a**)*

Yield: 2.23 g (70% relative to $[W(CO)_6]$). Dec. >166 °C. IR (THF, cm^{-1}): ν(C≡C) 2091 w, ν(CO) 1995 s, 1914 s, ν(C=O) 1687 m. ^{1}H-NMR ($CD_3C(O)CD_3$): $\delta = 2.29$ (s, 3H, C_6H_4-Me-*p*), 7.05–7.35 (m, 4H, C_6H_4-Me-*p*), 7.90 (dt, $^3J = 6.5$ Hz, $^4J = 1.1$ Hz, 2H, C3-H), 8.46 (dt, $^3J = 7.9$ Hz, $^4J = 1.4$ Hz, 2H, C5-H), 8.80 (d, $^3J = 8.3$ Hz, 2H, C4-H), 9.38 (d, $^3J = 5.5$ Hz, 2H, C6-H). ^{13}C-NMR ($CD_3C(O)CD_3$): $\delta = 21.5$ (C_6H_4-Me-*p*), 68.9 (C_β), 106.9 (C1, C_6H_4-Me-*p*), 118.9 (C_α), 124.6 (C3, bipy), 128.3 (C5, bipy), 130.3, 133.3, 140.3 (C_6H_4-Me-*p*), 142.1 (C4, bipy), 155.8 (C6, bipy), 156.3 (C2, bipy), 160.7 (q, $^2J = 35$ Hz, CF_3CO_2), 225.3 ($^1J(WC) = 170$ Hz, CO), 244.6 (W≡C). MS (FAB, THF/NBA): m/z (%) = 523 (1) $[M^+ - CF_3CO_2]$, 467 (1) $[M^+ - CF_3CO_2 - 2CO]$. Anal. Found: C, 45.52; H, 2.60; N, 3.72. Calc. for $C_{24}H_{15}F_3N_2O_4W$ (636.0): C, 45.31; H, 2.38; N, 4.40%.

*3.2.6. 2,2′-Bipyridyl(dicarbonyl)(trifluoroacetato)-(p-tolylpropynylidyne)molybdenum (**3b**)*

Yield: 1.51 g (55% relative to $[Mo(CO)_6]$). Dec. >143 °C. IR (THF, cm^{-1}): ν(C≡C) 2110 w; 2084 w, ν(CO) 2009 s, 1933 s, ν(C=O) 1703 m. ^{1}H-NMR ($CD_3C(O)CD_3$): $\delta = 2.30$ (s, 3H, C_6H_4-Me-*p*), 7.10–7.40 (m, 4H, C_6H_4-Me-*p*), 7.83 (dt, $^3J = 6.4$ Hz, $^4J = 1.0$ Hz, 2H, C3-H), 8.39 (dt, $^3J = 7.9$ Hz, $^4J = 1.7$ Hz, 2H, C5-H), 8.72 (d, $^3J = 8.0$ Hz, 2H, C4-H), 9.24 (dd, $^3J = 5.7$ Hz, $^4J = 1.8$ Hz, 2H, C6-H). ^{13}C-NMR ($CD_3C(O)CD_3$): $\delta = 21.5$ (C_6H_4-Me-*p*), 64.6 (C_β), 100.6 (C_1, C_6H_4-Me-*p*), 118.0 (C_α), 124.2 (C3, bipy), 127.5 (C5, bipy), 130.3, 133.8, 141.1 (C_6H_4-Me-p), 141.8 (C4, bipy), 155.3 (C6, bipy), 155.6 (C2, bipy), 226.5

(CO), 252.2 (Mo≡C). MS (FAB, THF/NBA): *m/z* (%) = 494 (1) [$M^+ - 2CO$], 435 (2) [$M^+ - CF_3CO_2$]. Anal. Found: C, 52.48; H, 2.92; N, 4.97. Calc. for $C_{24}H_{15}F_3MoN_2O_4$ (548.3): C, 52.57; H, 2.76; N, 5.11%.

*3.2.7. 2,2′-Bipyridyl(dicarbonyl)(trifluoroacetato)(t-butylpropynylidyne)tungsten (**4a**)*

Yield: 2.38 g (79% relative to [$W(CO)_6$]). Dec. > 214 °C. IR (THF, cm^{-1}): ν(C≡C) 2133 w, ν(CO) 1993 s, 1910 s, ν(C=O) 1690 m. ^{1}H-NMR ($CD_3C(O)CD_3$): $\delta = 1.13$ (s, 9H, CMe$_3$), 7.87 (dt, $^3J = 5.5$ Hz, $^4J = 1.2$ Hz, 2H, C3-H), 8.43 (dt, $^3J = 8.6$ Hz, $^4J = 1.7$ Hz, 2H, C5-H), 8.76 (dd, $^3J = 8.6$ Hz, $^4J = 1.2$ Hz, 2H, C4-H), 9.32 (dd, $^3J = 4.6$ Hz, $^4J = 0.8$ Hz, 2H, C6-H). ^{13}C-NMR ($CD_3C(O)CD_3$): $\delta = 30.6$ (CMe$_3$), 81.7 (C_α), 98.1 (C_β), 124.5 (C3, bipy), 128.2 (C5, bipy), 142.0 (C4, bipy), 155.6 (C6, bipy), 156.3 (C2, bipy), 225.3 (CO), 247.8 (W≡C). MS (FAB, THF/NBA): *m/z* (%) = 489 (1) [$M^+ - CF_3CO_2$], 433 (1) [$M^+ - CF_3CO_2 - 2CO$]. Anal. Found: C, 41.75; H, 3.02; N, 4.15. Calc. for $C_{21}H_{17}F_3N_2O_4W$ (602.2): C, 41.88; H, 2.85; N, 4.65%.

*3.2.8. Dicarbonyl(4,4′-dimethyl-2,2′-bipyridyl)(trifluoroacetato)(trimethylsilylpropynylidyne)–tungsten (**5a**)*

Yield: 2.65 g (82% relative to [$W(CO)_6$]). Dec. > 201 °C. IR (THF, cm^{-1}): ν(C≡C) 2055 w, ν(CO) 1998 s, 1916 s, ν(C=O) 1694 m. ^{1}H-NMR ($CD_3C(O)CD_3$): $\delta = 0.07$ (s, 9H, SiMe$_3$), 2.64 (s, 6H, C4-Me), 7.68 (d, $^3J = 5.3$ Hz, 2H, C5-H), 8.62 (s, 2H, C3-H), 9.14 (d, $^3J = 5.6$ Hz, 2H, C6-H). ^{13}C-NMR ($CD_3C(O)CD_3$): $\delta = 1.9$ (SiMe$_3$), 21.6 (C4-Me), 76.3 (C_β), 120.7 (C_α), 125.1 (C3, bipy), 128.8 (C5, bipy), 155.3 (C4, bipy), 155.5 (C6, bipy), 156.0 (C2, bipy), 160.6 (q, ^2J(CF) = 36 Hz, $CF_3\mathit{C}O_2$), 225.2 (^1J(WC) = 134 Hz, CO), 245.9 (^1J(WC) = 197 Hz, W≡C). MS (FAB, CH_2Cl_2/NBA): *m/z* (%) = 590 (4) [$M^+ - 2CO$], 533 (36) [$M^+ - CF_3CO_2$], 477 (17) [$M^+ - CF_3CO_2 - 2CO$], 185 (100) [$C_{12}H_{12}N_2 + H$]. Anal. Found: C, 40.38; H, 3.28; N, 4.04. Calc. for $C_{22}H_{21}F_3N_2O_4SiW$ (646.4): C, 40.88; H, 3.27; N, 4.33%.

*3.2.9. Dicarbonyl(4,4′-dimethyl-2,2′-bipyridyl)(trifluoroacetato)(trimethylsilylpropynylidyne)–molybdenum (**5b**)*

Yield: 1.87 g (67% relative to [$Mo(CO)_6$]). Dec. > 163 °C. IR (THF, cm^{-1}): ν(C≡C) 2050 w, ν(CO) 2013 s, 1935 s, ν(C=O) 1706 m. ^{1}H-NMR ($CD_3C(O)CD_3$): $\delta = 0.09$ (s, 9H, SiMe$_3$), 2.62 (s, 6H, C4-Me), 7.62 (d, $^3J = 5.2$ Hz, 2H, C5-H), 8.55 (s, 2H, C3-H), 9.01 (d, $^3J = 5.5$ Hz, 2H, C6-H). ^{13}C-NMR ($CD_3C(O)CD_3$): $\delta = -0.5$ (SiMe$_3$), 21.4 (C4-Me), 72.1 (C_β), 113.6 (C_α), 116.1 (q, ^1J(CF) = 292 Hz, CF_3CO_2), 124.6 (C3, bipy), 128.0 (C5, bipy), 154.2 (C4, bipy), 154.6 (C6, bipy), 155.3 (C2, bipy), 161.1 (q, ^2J(CF) = 38 Hz, CF_3CO_2), 226.3 (CO), 253.1 Mo≡C). MS (FAB, THF/NBA): *m/z* (%) = 504 (4) [$M^+ - 2CO$], 447 (8) [$M^+ - CF_3CO_2$], 391 (17) [$M^+ - CF_3CO_2 - 2CO$], 185 (40) [$C_{12}H_{12}N_2 + H$], 73 (76) [SiMe$_3$]. Anal. Found: C, 47.09; H, 3.75; N, 4.91. Calc. for $C_{22}H_{21}F_3N_2O_4SiW$ (558.4): C, 47.32; H, 3.79; N, 5.02%.

*3.2.10. Dicarbonyl(4,4′-dimethyl-2,2′-bipyridyl)(trifluoroacetato)(phenylpropynylidyne)tungsten (**6a**)*

Yield: 1.79 g (55% relative to [$W(CO)_6$]). Dec. > 162 °C. IR (THF, cm^{-1}): ν(CO) 1995 s, 1913 s, ν(C=O) 1704 m. ^{1}H-NMR ($CD_3C(O)CD_3$): $\delta = 2.65$ (s, 6H, C4-Me), 7.25–7.45 (m, 5H, Ph), 7.69 (d, $^3J = 5.3$ Hz, 2H, C5-H), 8.64 (s, 2H, C3-H), 9.18 (d, $^3J = 5.6$ Hz, 2H, C6-H). ^{13}C-NMR ($CD_3C(O)CD_3$): $\delta = 21.2$ (C4-Me), 67.9 (C_β), 106.6 (C1, Ph), 116.0 (q, $^1J = 290$ Hz, CF_3CO_2), 121.7 (C_α), 124.5 (C3, bipy), 128.3 (C5, bipy), 129.0, 129.2, 132.8 (Ph), 154.3 (C4, bipy), 154.6 (C6, bipy), 155.6 (C2, bipy), 160.1 (q, $^2J = 36$ Hz, CF_3CO_2), 225.0 (^1J(WC) = 170 Hz, CO), 243.4 (W≡C). MS (FAB, THF/NBA): *m/z* (%) = 622 (1) [$M^+ - CO$], 594 (3) [$M^+ - 2CO$], 537 (5) [$M^+ - CF_3CO_2$], 481 (4) [$M^+ - CF_3CO_2 - 2CO$], 185 (100) [$C_{12}H_{12}N_2 + 1$]. Anal. Found: C, 45.37; H, 3.06; N, 3.94. Calc. for $C_{25}H_{17}F_3N_2O_4W$ (650.3): C, 46.18; H, 2.64; N, 4.31%.

*3.2.11. Dicarbonyl(4,4′-dimethyl-2,2′-bipyridyl)(trifluoroacetato)(phenylpropynylidyne)molybdenum (**6b**)*

Yield: 2.05 g (73% relative to [$Mo(CO)_6$]). Dec. > 135 °C. IR (THF, cm^{-1}): ν(C≡C) 2096 w, ν(CO) 2009 s, 1932 s, ν(C=O) 1699 m. ^{1}H-NMR ($CD_3C(O)CD_3$): $\delta = 2.62$ (s, 6H, C4-Me), 7.25–7.50 (m, 5H, Ph), 7.63 (d, $^3J = 5.4$ Hz, 2H, C5-H), 8.55 (s, 2H, C3-H), 9.04 (d, $^3J = 5.5$ Hz, 2H, C6-H). ^{13}C-NMR ($CD_3C(O)CD_3$, 62.9 MHz): $\delta = 21.5$ (C4-Me), 64.1 (C_β), 100.7 (C1, Ph), 119.2 (C_α), 124.7 (C3, bipy), 128.1 (C5, bipy), 129.6, 130.3, 133.7 (Ph), 154.2 (C4, bipy), 154.6 (C6, bipy), 155.4 (C2, bipy), 160.9 (q, $^2J = 35$ Hz, CF_3CO_2), 226.6 (CO), 251.3 (Mo≡C). MS (FAB, THF/NBA): *m/z* (%) = 508 (10) [$M^+ - 2CO$], 451 (12) [$M^+ - CF_3CO_2$], 395 (17) [$M^+ - CF_3CO_2 - 2CO$], 185 (88) [$C_{12}H_{12}N_2 - 1$], 78 (60) [SiMe$_3$ + 1]. Anal. Found: C, 53.16; H, 3.25; N, 4.73. Calc. for $C_{25}H_{17}F_3MoN_2O_4$ (562.4): C, 53.40; H, 3.05; N, 4.98%.

*3.2.12. Dicarbonyl(4,4′-dimethyl-2,2′-bipyridyl)(trifluoroacetato)(p-tolylpropynylidyne)tungsten (**7a**)*

Yield: 2.23 g (67% relative to [$W(CO)_6$]). Dec. > 173 °C. IR (THF, cm^{-1}): ν(CO) 1994 s, 1912 s, ν(C=O) 1708 m. ^{1}H-NMR ($CD_3C(O)CD_3$): $\delta = 2.28$ (s, 3H, C_4H_6-Me-*p*), 2.65 (s, 6H, C_4Me), 7.05–7.30 (m, 5H, C_6H_4-Me-*p*), 7.69 (d, $^3J = 4.2$ Hz, 2H, C5-H), 8.63 (s, 2H, C3-H), 9.17 (d, $^3J = 5.7$ Hz, 2H, C6-H). ^{13}C-NMR ($CD_3C(O)CD_3$): $\delta = 21.5$ (C_4Me), 21.6 (C_6H_4-Me), 68.8 (C_β), 106.9 (C1, C_6H_4-Me-*p*), 117.2 (q, $^1J = 290$ Hz, CF_3CO_2), 119.0 (C_α), 125.0 (C3, bipy), 128.8 (C5, bipy);

130.2, 133.2, 140.2 (C_6H_4-Me-p), 154.7 (C4, bipy), 155.0 (C6, bipy), 156.1 (C2, bipy), 160.7 (q, $^2J = 36$ Hz, CF_3CO_2), 225.6 (^1J(WC) = 170 Hz, CO), 244.3 (^1J(WC) = 198 Hz, W≡C). MS (FAB, THF/NBA): m/z (%) = 636 (2) [$M^+ - CO$], 608 (2) [$M^+ - 2CO$], 551 (5) [$M^+ - CF_3CO_2$], 495 (4) [$M^+ - CF_3CO_2 - 2CO$], 185 (45) [$C_{12}H_{12}N_2 + 1$]. Anal. Found: C, 47.21; H, 2.65; N, 4.48. $C_{26}H_{19}F_3N_2O_4W$ (664.3): C, 47.01; H, 2.88; N, 4.22%.

3.2.13. *Dicarbonyl(4,4′-dimethyl-2,2′-bipyridyl)(trifluoroacetato)(p-tolylpropynylidyne)molybdenum (**7b**)*

Yield: 1.79 g (62% relative to [$Mo(CO)_6$]). Dec. > 156 °C. IR (THF, cm^{-1}): ν(C≡C) 2110 vw, 2083 vw, ν(CO) 2007 s, 1931 s, ν(C=O) 1700 m. ^{1}H-NMR ($CD_3C(O)CD_3$): $\delta = 2.30$ (s, 3H, C_4H_6-Me-*p*), 2.62 (s, 6H, C_4Me), 7.05–7.35 (m, 5H, C_6H_4-Me-*p*), 7.63 (d, $^3J = 5.2$ Hz, 2H, C5-H), 8.56 (s, 2H, C3-H), 9.04 (d, $^3J = 5.6$ Hz, 2H, C6-H). ^{13}C-NMR ($CD_3C(O)CD_3$): $\delta =$ 21.5 (C_4Me), 21.5 (C_6H_4-Me-*p*), 64.5 (C_β), 100.6 (C1, C_6H_4-Me-*p*), 116.9 (q, $^1J = 290$ Hz, CF_3CO_2), 118.1 (C_α), 124.7 (C3, bipy), 128.0 (C5, bipy), 130.3, 133.7, 141.0 (C_6H_4-Me-p), 154.2 (C4, bipy), 154.6 (C6, bipy), 155.4 (C2, bipy), 160.8 (q, $^2J = 35$ Hz, CF_3CO_2), 226.7 (CO), 251.8 (Mo≡C). MS (FAB, THF/NBA): m/z (%) = 522 (2) [$M^+ - 2CO$], 465 (3) [$M^+ - CF_3CO_2$], 409 (3) [$M^+ - CF_3CO_2 - 2CO$]. Anal. Found: C, 52.28; H, 3.43; N, 4.41. Calc. for $C_{26}H_{19}F_3MoN_2O_4$ (576.4): C, 54.18; H, 3.32; N, 4.86%.

3.3. *Determination of equilibrium constants*

Solutions obtained by dissolving the appropriate amount of the complexes (0.03–0.12 g, 0.05–0.27 mmol) in 0.5 ml of THF were stepwise diluted with THF. The amount of complex depended on the solubility in THF. The concentration of each solution was calculated and an IR spectrum taken. Partially overlapping absorptions of A_1 and A_1^* (B_1 and B_1^*) ν(CO) absorptions were analyzed using the computer program ‘PEAKFIT’ (Jandel Scientific). The intensity of the B_1 and B_1^* absorption thus obtained was used in the calculation of the equilibrium constants K. The initial formation of dimers was assumed: ($K = [\text{dimer}]/[\text{monomer}]^2$).

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References

[1] (a) E.O. Fischer, G. Kreis, C.G. Kreiter, J. Müller, G. Huttner, H. Lorenz, Angew. Chem. 85 (1973) 618;
(b) E.O. Fischer, G. Kreis, C.G. Kreiter, J. Müller, G. Huttner, H. Lorenz, Angew. Chem. Int. Ed. Engl. 12 (1973) 564.

[2] E.O. Fischer, H.J. Kalder, F.H. Köhler, J. Organomet. Chem. 81 (1974) C23.

[3] (a) I.J. Hart, A.F. Hill, F.G.A. Stone, J. Chem. Soc. Dalton Trans. (1989) 2261.;
(b) S.J. Dossett, I.J. Hart, F.G.A. Stone, J. Chem. Soc. Dalton Trans. (1990) 3481.

[4] B. Schwenzer, J. Schleu, N. Burzlaff, C. Karl, H. Fischer, J. Organomet. Chem. 641 (2002) 134.

[5] A. Mayr, G.A. McDermott, A.M. Dorries, Organometallics 4 (1985) 608.

[6] Crystallographic data for **8a** and **10a** may be obtained free of charge from the Cambridge Crystallographic Data Centre, CCDC nos. 166389 (**8a**) and 166390 (**10a**) [The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk)].

[7] Z. Xu, A. Mayr, I.S. Butler, J. Organomet. Chem. 648 (2002) 93–98.

[8] M. Pui Yin Yu, A. Mayr, K.-K. Cheung, J. Chem. Soc. Dalton Trans. (1998) 475.

[9] E.O. Fischer, W. Röll, N. Hoa Tran Huy, K. Ackermann, Chem. Ber. 115 (1982) 2951.

[10] F.-W. Lee, M.C.-W. Chan, K.-K. Cheung, C.-M. Che, J. Organomet. Chem. 563 (1998) 191.