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Unsaturated alkylidyne ligands bearing a terminal isocyanide functionality and intervening ethynylbenzene groups

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Abstract

The synthesis of complexes **2** [W(CC_6H_4($CCC_6H_4NH_2$-4)-4)Cl$(CO)_2$(dppe)], and **4** [W(CC_6H_4(CCC_6H_4($CCC_6H_2iPr_2$-3,5-NHCHO-4)-4)-4)Cl$(CO)_2$(dppe)], was achieved by Pd(II) catalyzed cross-coupling reactions of complex **1** [W(CC_6H_4I-4)Cl$(CO)_2$(dppe)], with the respective aromatic acetylenes. Formylation of complex **2** with acetic formic anhydride affords the formamide **3** [W(CC_6H_4(CCC_6H_4NHCHO-4)-4)Cl$(CO)_2$(dppe)]. The isocyanide derivatives **5** [W(CC_6H_4(CCC_6H_4NC-4)-4)Cl$(CO)_2$(dppe)], and **6** [W(CC_6H_4(CCC_6H_4($CCC_6H_2iPr_2$-3,5-NC-4)-4)-4)Cl$(CO)_2$(dppe)], were obtained by dehydration of complexes **3** and **4** with triphosgene/NEt_3.

Keywords: Metal alkylidyne; Isocyanide; Tungsten

1. Introduction

In unsaturated alkylidyne metal complexes [1] the metal–carbon triple bond establishes a strong electronic connection between transition metal centers and organic π systems [2]. This feature is of potential utility for the development of molecular materials whose function depends on the electronic communication between distant metal centers across unsaturated organic ligands [3,4]. As a potential means of attaching additional metal centers to unsaturated alkylidyne ligands in a π-conjugated manner, we are exploring the effectiveness of the isocyanide functionality[5,6]. In the course of these efforts, we have recently developed tungsten complexes of the 4-isocyanobenzylidyne ligand [7]. For a systematic exploration of distance effects on the electronic communication between π-conjugated metal centers across extended unsaturated ligands, it would be desirable to have extended analogues of the isocyanobenzylidyne ligand available. The synthesis of such ligands has been made possible by the recent demonstration of palladium-catalyzed cross-coupling reactions of the 4-iodobenzylidyne ligand [8]. Here we report the application of this reaction towards the synthesis of extended isocyanobenzylidyne ligands bearing one or two intervening ethynylbenzene groups.

2. Results and discussion

The amino-substituted extended benzylidyne tungsten complex **2** was synthesized by palladium-catalyzed cross-coupling [9] of the 4-iodobenzylidyne complex **1** with 4-aminoethynylbenzene (Eq. (1), Scheme 1). As a result of treatment with formic acetic anhydride, complex **2** is then transformed into the formamide derivative **3**, which is subsequently dehydrated with triphosgene/NEt_3 to give the isocyanide derivative **5** (Eqs. (2) and (3)) [10]. For the synthesis of the extended formamide **4**, 4-(4-formamido-3,5-diisopropylethynyl-

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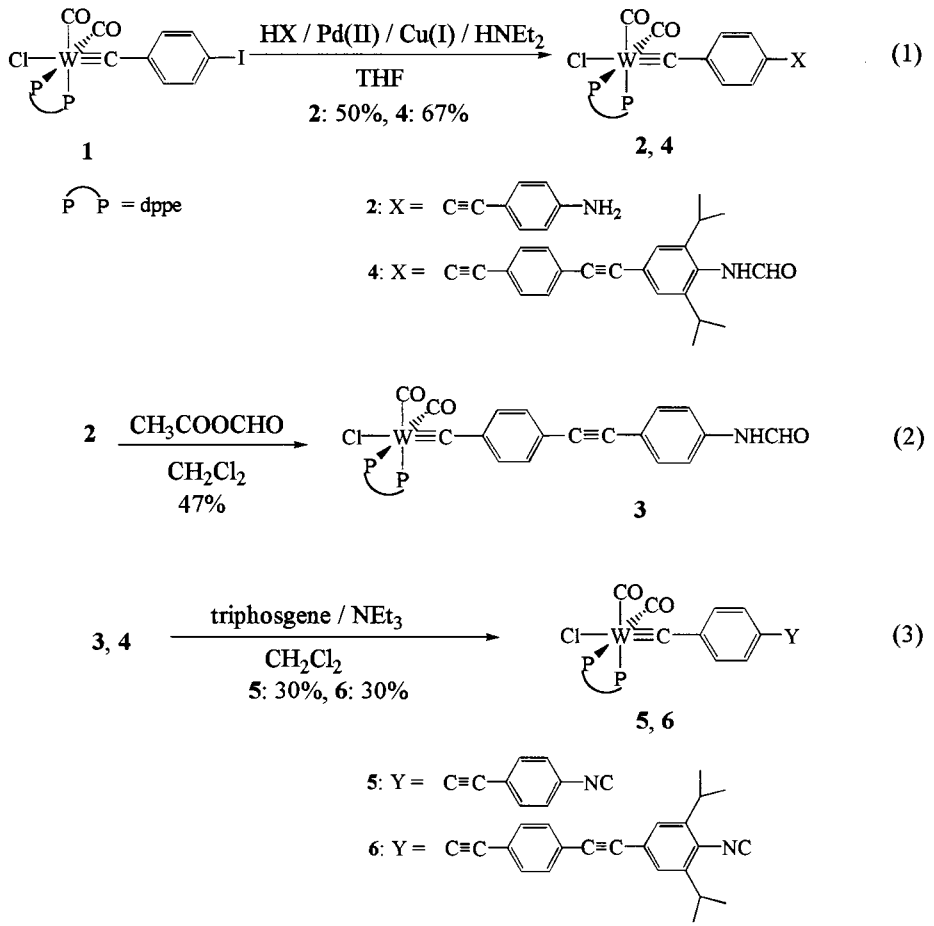

Scheme 1.

benzene)-ethynylbenzene [11] is employed in the cross-coupling step (Eq. (1)). The formamide **4** is then dehydrated to afford the isocyanide **6** (Eq. (3)). The alkylidyne ligands of complexes **5** and **6** may be considered as extended 4-isocyanobenzylidynes containing one and two intervening ethynylbenzene groups, respectively. Complexes **5** and **6**, both containing free isocyanide groups, appear to be stable compounds. No signs of decomposition were observed upon handling of the compounds at room temperature (r.t.) under a nitrogen atmosphere in the solid state or in solution. However, for long-term storage, the compounds were kept in a refrigerator. The free isocyanide groups of complexes **5** and **6** gave rise to strong absorptions in the IR at about 2125 cm^{-1} [5]. Weak IR absorptions for the ethynyl groups at about 2204–2214 cm^{-1} could be discerned for complexes **2**, **5** and **6**. The IR stretching frequencies of the two *cis*-carbonyl ligands of all new complexes are very similar and occur at about 2007 and 1937 cm^{-1}. The variations in the carbonyl stretching frequencies between the different compounds are too small to indicate any influence of the remote functional groups on the electron density of the tungsten complex fragment. In contrast, the transformation of the amino group of the parent 4-aminobenzylidyne ligand in $[W(CC_6\text{-}H_4NH_2\text{-}4)Cl(CO)_2(tmeda)]$ (tmeda = tetramethylethylenediamine) into the isocyano group caused a shift in the carbonyl stretching frequencies to a higher energy by about 10 cm^{-1} [7]. Although this shift is relatively small, it indicates substantial ground state electronic communication between the alkylidyne metal center and functional groups across the benzylidyne ligand, particularly considering that the carbonyl ligands are primarily interacting with that metal d orbital which is orthogonal to the π system of the alkylidyne ligand [2]. Similarly, the ^{13}C-NMR resonance of the alkylidyne carbon atom of all the new compounds **2**–**6** occurred in a very narrow range, from δ 263 to 266, while the alkylidyne carbon resonances of the parent 4-aminobenzylidyne and 4-isocyanobenzylidyne ligands differ by 7–8 ppm. Thus in the extended benzylidyne ligands reported here, any influence of the remote functional groups on the electron density of the metal center is apparently too small to be discerned by IR or NMR. The insulating influence of intervening ethynylbenzene groups on ground-state electronic interactions between remote functional groups in extended conjugated π systems has previously been noted [12]. Nevertheless,

ethynylbenzene groups have been employed successfully as spacer groups for the construction of molecular materials whose function involves electronic excitation, reduction, or oxidation [13]. Extended benzylidyne ligands of the type presented here may therefore be expected to be of use in establishing long-range electronic interactions between remote metal centers. The versatility of the isocyanide functionality as a coordinating group [5] ensures that the alkylidyne metal centers in complexes **5** and **6** can be paired with a diverse variety of metal complex fragments.

3. Experimental section

Standard inert atmosphere techniques were used throughout. Diethyl ether, hexane and THF were purified by reflux over sodium and distilled under nitrogen. Methylene chloride was heated to reflux over calcium hydride and distilled under nitrogen. Compound **1** [8] and 4-aminoethynylbenzene ([9]d) were synthesized according to the reported procedures. The compounds *cis*-$PdCl_2(PPh_3)_2$ and CuI were obtained from commercial sources.

^{1}H-, ^{13}C- and ^{31}P-NMR spectra were recorded on 270 MHz JEOL JNMGSX270 FT-NMR, 300 MHz BRUKER DPX300 FT-NMR and 500 MHz BRUKER DRX500 FT-NMR spectrometers. ^{1}H- and ^{13}C-NMR chemical shifts are given in ppm (δ) relative to TMS. ^{31}P-NMR spectra are referenced to 85% H_3PO_4 and are proton decoupled. IR spectra were recorded on a Shimadzu FTIR-8201PC spectrometer. Melting points were recorded on a Stuart Scientific SMP1 instrument under nitrogen. Elemental analyses were performed by Butterworth Laboratories Ltd.

3.1. *[W(CC$_6$H$_4$(CCC$_6$H$_4$NH$_2$-4)-4)Cl(CO)$_2$(dppe)] (**2**)*

Complex **1** (0.444 g, 0.5 mmol) was dissolved in THF (30 ml) and $HNEt_2$ (1 ml) was added. To this solution 4-$HCCC_6H_4NH_2$ (20% excess, 0.14 g), *cis*-$PdCl_2(PPh_3)_2$ (10 mg) and CuI (20 mg) were added. The resulting mixture was stirred at r.t. overnight. The solvent was then removed in vacuo. The residue was washed with hexane, dried, and redissolved in CH_2Cl_2. After filtration, hexane was added to the solution to afford yellow–orange micro-crystals of **2** (0.44 g, 50%), m.p. 190–193°C (dec.). ^{1}H-NMR ($CDCl_3$): δ 7.73–7.20 (22H, P*Ph*$_2$, $C_6H_4NH_2$), 7.05 (d, $J = 8.23$ Hz, 2H, C_6H_4CC), 6.62 (d, $J = 8.46$ Hz, 2H, $C_6H_4NH_2$), 6.43 (d, $J = 8.23$ Hz, 2H, C_6H_4CC), 3.86 (br, 2H, NH_2), 2.94–2.90 (m, 2H, CH_2PPh$_2$), 2.65–2.63 (m, 2H, CH_2PPh$_2$). ^{13}C-NMR ($CDCl_3$): δ 266.0 (W≡*C*), 212.4 (*C*O, $^1J_{PC}^{cis} = 7$ Hz, $^1J_{PC}^{trans} = 45$ Hz), 148.1, 146.8, 135.7, 135.4, 133.0, 132.9, 132.7, 132.6, 132.5, 132.4, 132.1, 130.8, 130.2, 130.1, 129.4, 128.7, 128.6, 128.5, 122.5, 114.8, 112.5 (P*Ph*$_2$, C_6H_4CC, $C_6H_4NH_2$), 92.6, 87.9 (*C*≡*C*), 27.4, 27.3, 27.2, 27.1 (*C*H$_2$PPh$_2$). ^{31}P-NMR ($CDCl_3$): δ 38.6 ($^1J_{WP} = 231$ Hz). IR (CH_2Cl_2, cm^{-1}): 2204 (w, ν_{CC}), 2008 (s, ν_{CO}), 1938 (s, ν_{CO}). Anal. Found: C, 56.57; H, 3.59; N, 1.50. $C_{43}H_{34}ClNO_2P_2W \cdot 1/2CH_2Cl_2$. Calc. C, 56.76; H, 3.83; N, 1.52%.

3.2. *[W(CC$_6$H$_4$(CCC$_6$H$_4$NHCHO-4)-4)Cl(CO)$_2$(dppe)] (**3**)*

Complex **2** (1 mmol, 0.877 g) was dissolved in THF (50 ml), and 0.1 ml acetic formic anhydride was added at 0°C. The resulting mixture was stirred at 0°C for 15 min, the solvent was then removed in vacuo. The residue was washed with anhydrous ether, dried, and redissolved in CH_2Cl_2. After filtration, hexane was added to the solution to afford yellow–orange microcrystals of **3** (0.425 g, 47%), m.p. 147–150°C (dec.). ^{1}H-NMR (acetone-d_6): δ 9.44 (s, 1H, NHC*H*O, major isomer), 9.30 (d, $J = 10.45$ Hz, NHC*H*O, minor isomer), 8.91 (d, $J = 10.96$ Hz, N*H*CHO, minor isomer), 8.40 (s, 1H, N*H*CHO, major isomer), 7.99–7.20 (24H, P*Ph*$_2$, C_6H_4NHCHO), 7.15 (d, $J = 8.28$ Hz, 2H, C_6H_4CC), 6.53 (d, $J = 8.23$ Hz, 2H, C_6H_4CC), 3.17–3.05 (m, 2H, CH_2PPh$_2$), 2.98–2.86 (m, 2H, CH_2PPh$_2$). ^{13}C-NMR (acetone-d_6): δ 265.3 (W≡*C*), 214.7 (*C*O, $^1J_{PC}^{cis} = 7$ Hz, $^1J_{PC}^{trans} = 46$ Hz), 160.1 (NH*C*HO), 149.6, 139.7, 139.6, 136.8, 136.5, 133.9, 133.6, 133.5, 133.4, 133.0, 131.6, 131.3, 131.1, 131.0, 130.3, 129.5, 129.3, 129.2, 127.7, 122.8, 120.1, 118.9, 118.4, 118.3 (P*Ph*$_2$, C_6H_4CC, C_6H_4NHCHO), 92.4, 89.8 (*C*≡*C*), 27.5, 27.4, 27.3, 27.2 (*C*H$_2$PPh$_2$). ^{31}P-NMR ($CDCl_3$): δ 38.7 ($^1J_{WP} = 231$ Hz). IR (CH_2Cl_2, cm^{-1}): 2006 (s, ν_{CO}), 1940 (s, ν_{CO}).

3.3. *[W(CC$_6$H$_4$(CCC$_6$H$_4$(CCC$_6$H$_2$*i*Pr$_2$-3,5-NHCHO-4)-4)-4)Cl(CO)$_2$(dppe)] (**4**)*

The synthesis follows the procedure described for **2**, whereby **1** (0.888 g) and $HCCC_6H_4$(CCC$_6$H$_2$*i*Pr$_2$-3,5-NHCHO-4)-4 [11] (0.395 g) were used. Yellow microcrystals. Yield: 0.73 g, 67%, m.p. 165–168°C (dec.). ^{1}H-NMR ($CDCl_3$): δ 8.48 (s, 1H, NHC*H*O, minor isomer), 8.04 (d, $J = 11.90$ Hz, 1H, NHC*H*O, major isomer), 7.74–7.20 (26H, P*Ph*$_2$, C_6H_4, C_6H_2*i*Pr$_2$), 7.10 (d, $J = 8.12$ Hz, 2H, CC$_6H_4$), 6.93 (d, $J = 12.00$ Hz, 1H, NHC*H*O, major isomer), 6.77 (s, 1H, NHC*H*O, minor isomer), 6.45 (d, $J = 8.20$ Hz, 2H, CC$_6H_4$), 3.25–2.86 (4H, CH_2PPh$_2$, C*H*(CH$_3$)$_2$), 2.74–2.59 (2H, CH_2PPh$_2$), 1.30–1.23 (12H, CH_3). ^{13}C-NMR ($CDCl_3$): δ 265.1 (W≡*C*), 212.4 (*C*O, $^1J_{PC}^{trans} = 52$ Hz), 164.8 (NH*C*HO, major isomer), 160.5 (NH*C*HO, minor isomer), 148.8, 146.9, 146.5, 135.8, 135.2, 133.0, 132.9, 132.8, 132.7, 132.6, 132.5, 132.1, 131.6, 131.4, 130.6, 130.3, 130.2, 130.0, 129.4, 128.9, 128.6, 128.5, 127.3, 127.2, 127.1,

123.5, 123.3, 123.2, 123.0, 122.9, 121.4, 121.3 (P*Ph*$_2$, C*C*$_6$H$_4$CC, *C*$_6$H$_4$, *C*$_6$H$_2$*i*Pr$_2$), 91.9, 91.6, 91.3, 91.0, 89.5, 89.0 (*C*≡*C*), 31.6, 28.8 (*C*H(CH$_3$)$_2$), 27.5, 27.4, 27.2, 27.0 (*C*H$_2$PPh$_2$), 23.5, 22.7 (*C*H$_3$). ^{31}P-NMR (CDCl$_3$): δ 39.2 ($^1J_{WP} = 231$ Hz). IR (CH$_2$Cl$_2$, cm^{-1}): 2008 (s, ν_{CO}), 1940 (s, ν_{CO}).

3.4. [W(CC$_6$H$_4$(CCC$_6$H$_4$NC-4)-4)Cl(CO)$_2$(dppe)] (5)

Complex **3** (1 mmol, 0.908 g) was dissolved in CH$_2$Cl$_2$ (50 ml), and 0.56 ml NEt$_3$ was added. After cooling to −78°C, a solution of triphosgene (C$_3$Cl$_6$O$_3$) (0.2 g) in CH$_2$Cl$_2$ (10 ml) was added. The resulting mixture was allowed to warm up to 0°C, and it was stirred at 0°C for 30 min. The solvent was then removed in vacuo. The residue was washed with hexane, then redissolved in THF (30 ml) and filtered. The solvent was again removed in vacuo. The residue was redissolved in CH$_2$Cl$_2$. After filtration, hexane was added to the solution to afford yellow–orange crystals of **5** (0.266 g, 30%), m.p. 135–138°C (dec.). ^{1}H-NMR (CDCl$_3$): δ 7.75–7.13 (24H, P*Ph*$_2$, C$_6$H$_4$NC), 7.10 (d, $J = 8.30$ Hz, 2H, C$_6$*H*$_4$CC), 6.46 (d, $J = 8.31$ Hz, 2H, C$_6$*H*$_4$CC), 2.96–2.88 (m, 2H, C*H*$_2$PPh$_2$), 2.71–2.63 (m, 2H, C*H*$_2$PPh$_2$). ^{13}C-NMR (CDCl$_3$): δ 264.6 (W≡*C*), 212.3 (*C*O, $^1J_{PC}^{cis} = 6$ Hz, $^1J_{PC}^{trans} = 46$ Hz), 165.9 (N≡*C*), 149.2, 135.9, 135.3, 133.0, 132.8, 132.7, 132.5, 132.4, 132.1, 131.0, 130.7, 130.3, 130.1, 129.8, 129.7, 129.5, 129.2, 128.6, 128.5, 128.4, 128.3, 128.1, 126.5, 126.2, 125.9, 124.7, 121.1, 120.7 (P*Ph*$_2$, *C*$_6$H$_4$NC, *C*$_6$H$_4$CC), 92.6, 89.8 (*C*≡*C*), 27.6, 27.4, 27.2, 27.0 (*C*H$_2$PPh$_2$). ^{31}P-NMR (CDCl$_3$): δ 38.5 ($^1J_{WP} = 231$ Hz). IR (CH$_2$Cl$_2$, cm^{-1}): 2214 (w, ν_{CC}), 2125 (m, ν_{CN}), 2006 (s, ν_{CO}), 1940 (s, ν_{CO}). Anal. Found: C, 58.48; H, 3.31; N, 1.68. C$_{44}$H$_{32}$ClNO$_2$P$_2$W·1/4CH$_2$Cl$_2$. Calc. C, 58.45; H, 3.60; N, 1.54%.

3.5. [W(CC$_6$H$_4$(CCC$_6$H$_4$(CCC$_6$H$_2$*i*Pr$_2$-3,5-NC-4)-4)-4)Cl(CO)$_2$(dppe)] (6)

The synthesis follows the procedure described for **5**, whereby **4** (0.27 g) was used. (Amounts of solvent and reagents same as described for **5**). Yellow micro-crystals. Yield: 0.10 g, 27%, m.p. 125–128°C (dec.). ^{1}H-NMR (CDCl$_3$): δ 7.73–7.67 (8H, P*Ph*$_2$), 7.52 (d, $J = 8.34$ Hz, 2H, C$_6$*H*$_4$), 7.48 (d, $J = 8.38$ Hz, 2H, C$_6$*H*$_4$), 7.40–7.21(14H, P*Ph*$_2$, C$_6$*H*$_2$*i*Pr$_2$), 7.10 (d, $J =$ 8.24 Hz, 2H, CC$_6$*H*$_4$), 6.46 (d, $J = 8.23$ Hz, 2H, CC$_6$*H*$_4$), 3.41–3.35 (m, 2H, C*H*(CH$_3$)$_2$), 3.00–2.88 (m, 2H, C*H*$_2$PPh$_2$), 2.71–2.59 (m, 2H, C*H*$_2$PPh$_2$), 1.30 (d, 12H, C*H*$_3$). ^{13}C-NMR (CDCl$_3$): δ 265.0 (W≡*C*), 212.3 (*C*O, $^1J_{PC}^{cis} = 8$ Hz, $^1J_{PC}^{trans} = 46$ Hz), 170.0 (N≡*C*), 148.9, 145.3, 135.8, 135.2, 132.9, 132.8, 132.7, 132.5, 132.1, 131.6, 131.5, 130.6, 130.3, 130.1, 129.4, 128.8, 128.6, 128.5, 126.7, 124.1, 124.0, 123.4, 122.6, 121.2 (P*Ph*$_2$, C*C*$_6$H$_4$CC, *C*$_6$H$_4$, *C*$_6$H$_2$*i*Pr$_2$), 92.0, 91.2, 90.7 (*C*≡*C*), 29.8 (*C*H(CH$_3$)$_2$), 27.5, 27.4, 27.1, 27.0 (*C*H$_2$PPh$_2$), 22.5 (*C*H$_3$). ^{31}P-NMR (CDCl$_3$): δ 39.2 ($^1J_{WP} = 231$ Hz). IR (CH$_2$Cl$_2$, cm^{-1}): 2206 (w, ν_{CC}), 2120 (m, ν_{CN}), 2008 (s, ν_{CO}), 1940 (s, ν_{CO}).

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