nitrogen using standard Schlenk techniques and were monitored by solution IR spectroscopy (carbonyl stretching region). Compound 1 was prepared as described previously;[7] ^{13}CO-enriched 1 was made from ^{13}CO-enriched $[Ru_3(CO)_{12}]$.[10] Infrared spectra were recorded on a Perkin-Elmer FT 1720-X spectrophotometer, using 0.1-mm CaF_2 cells. ^1H and ^{13}C NMR spectra were run with Bruker AC-200 and AC-300 instruments, using internal $SiMe_4$ as standard (δ = 0 ppm). Microanalyses were obtained from the University of Oviedo Analytical Service. Analysis of the products of the catalytic reactions was carried out on a Perkin-Elmer 8600 gas chromatograph, equipped with a 12-m AQ2 capillary column (i.d. 0.22 mm) and a flame ionization detector, at 160 °C; quantification was achieved with a PE-Nelson 1020 integrator.

Reaction of Compound 1 with Diphenylacetylene. A THF (10 mL) solution of complex 1 (103 mg, 0.156 mmol) and diphenylacetylene (56 mg, 0.312 mmol) was stirred at reflux temperature for 35 min. The solvent was removed under reduced pressure and the residue dissolved in toluene (1 mL). The resulting solution was chromatographed on a neutral alumina column (10 × 3 cm, activity IV). Orange and yellow bands were eluted with 4:1 and 2:1 hexane–dichloromethane, respectively, but they only contained trace amounts of compounds which could not be identified.[8] Dichloromethane eluted a pale-yellow fraction, while a brown residue remained uneluted at the top of the column. The pale-yellow fraction was evaporated to dryness to give, after crystallization from dichloromethane–hexane, $[Ru_2(\mu\text{-}C_8H_{11}N_2)(\mu\text{-}\eta^1,\eta^2\text{-}PhC{=}C(H)Ph)(CO)_5]$ (**2**) as an off-white solid (35 mg, 33% based on Ru). Anal. Found: C, 49.53; H, 3.62; N, 4.43. Calcd for $C_{27}H_{22}N_2O_5Ru_2$: C, 49.39; H, 3.38; N, 4.27. ν(CO) (*n*-pentane): 2052 m, 2006 s, 1992 m, 1959 m, 1939 m, cm^{-1}. ^1H NMR (C_6D_6, 200 MHz, 23 °C): 7.8–6.7 (m, phenyl protons), 6.29 (s, 1H), 6.06 (s, 1H) 3.73 (s, 1H, alkenyl C*H*), 3.08 (AB spin system, 2H, NH_2), 2.47 (s, 1H, N*H*), 1.85 (s, 3H, Me), 1.80 (s, 3H, Me) ppm. Selected $^{13}C\{^1H\}$ NMR data (CD_2Cl_2, 75.5 MHz, −40 °C, sample enriched in ^{13}CO): 204.6, 204.1, 201.1, 199.5, 196.4, (5 CO ligands), 80.2 (alkenyl *C*H), 19.6, 19.1 (2 Me), ppm.

Reaction of Compound 1 with Hydrogen. Hydrogen was bubbled through a solution of complex 1 in refluxing THF (20 mL) for 2.2 h. Since no reaction was observed by IR spectroscopy, the solvent was removed under reduced pressure, toluene (15 mL) added, and hydrogen bubbled through the resulting solution at reflux temperature (110 °C) for 2.5 h. After removal of the toluene, CD_2Cl_2 (1 mL) was added to give an insoluble residue and a solution whose ^1H NMR spectrum showed it to be a mixture of compounds with no peaks in the hydride region.

Catalytic Hydrogenation Reactions. The evolution of the catalytic reactions (Figure 1) was followed by gas chromatography. Reaction rates were obtained by measuring the hydrogen consumption as a function of time in a conventional gas buret.

The appropriate amounts of 1 and diphenylacetylene were placed in a two-necked 25-mL flask with one neck connected to the gas buret, which was in turn connected to a vacuum line. The flask was closed by a silicone septum and the system evacuated and filled with hydrogen five times. Degassed toluene (10 mL) was then introduced into the flask and the required pressure adjusted in the gas buret. The flask was immersed in a thermostated bath and shaken during the run at 600 min^{-1} with a Selecta shaker. An equilibration time of 2 min was allowed before acquiring any data. The working partial pressure of hydrogen was determined by subtracting the toluene vapor pressure at each temperature from the measured total pressure. Plots of the kinetic data were fitted using conventional regression programs.

Acknowledgment. We thank Dr. Miguel A. Esteruelas (University of Zaragoza, Zaragoza, Spain) for advice with the kinetic measurements. This work was supported by the CICYT (Spain), Project MAT90-0173. A.L. and J. M.F.-C. are grateful to the FICYT (Asturias, Spain) and the Ministerio de Educación y Ciencia (Spain) for postgraduate fellowships.

Registry No. 1, 126751-75-5; Ru, 7440-18-8; diphenylacetylene, 501-65-5; *cis*-stilbene, 645-49-8; 4,5-dimethyl-1,2-benzenediamine, 3171-45-7.

OM920289W

Preference of Carbonyl Ligands over Isocyanide Ligands in Nucleophile-Induced Coupling with Alkylidyne Ligands

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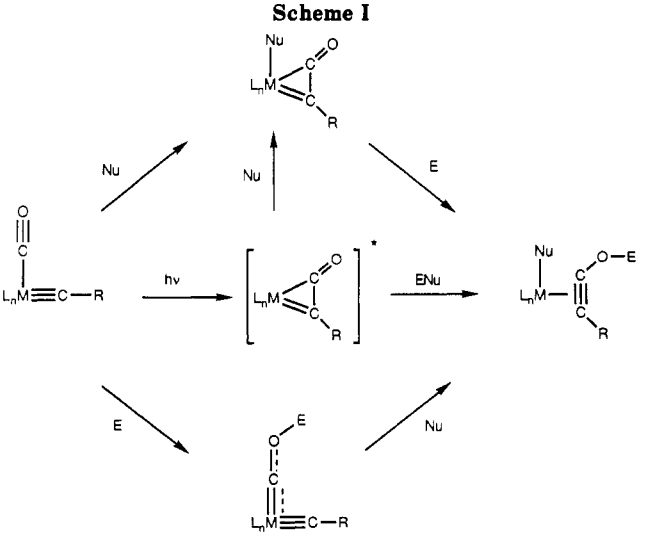
Summary: $W(CPh)Cl(CNCMe_3)_2(CO)_2$ was prepared by reaction of $W(CPh)Cl(CO)_2(py)_2$ with $CNCMe_3$ in CH_2Cl_2. $W(CPh)I(CNCMe_3)_2(CO)_2$ was prepared by sequential reaction of $W(CPh)Cl(CO)_2(py)_2$ with NaI in THF and with $CNCMe_3$ in CH_2Cl_2. Reaction of $W(CPh)Cl(CNCMe_3)_2(CO)_2$ with pyrrole-2-carboxaldehyde methylimine in the presence of KOH in THF gives the ketenyl complex $K[W(C_6H_7N_2)_2(PhCCO)(CO)]$. Reaction of $W(CPh)I(CNCMe_3)_2(CO)_2$ with NaS_2CNEt_2 in THF gives a mixture of products, of which $Na[W(PhCCO)(S_2CNEt_2)_2(CO)]$ is the main product. Reaction of $W(CPh)Cl(CNCMe_3)(CO)(PMe_3)_2$ with NaS_2CNEt_2 in THF leads to the formation of $[W(PhCCO)(S_2CNEt)_2(CO)(PMe_3)_2]$ and $[W(CPh)(S_2CNEt_2)(CO)(PMe_3)_2]$ as the main products.

Introduction

In a recent review article[1] we distinguished three fundamentally different types of alkylidyne–carbonyl coupling:[2] nucleophile-, electrophile-, and light-induced (Scheme I). Nucleophile-induced coupling (upper path-

Scheme I



† NSF-REU student from Southwest Texas State University, San Marcos, TX 78666, Summer 1991.

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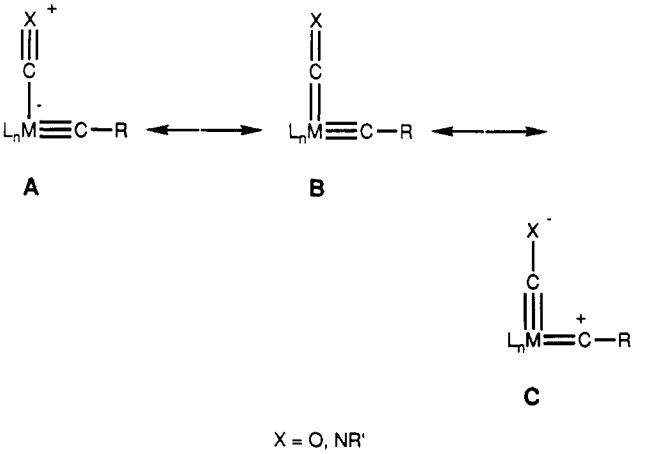
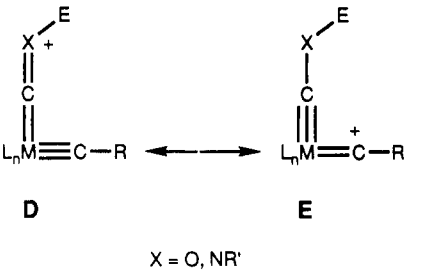
way in Scheme I) is very well established.[3] There is some experimental evidence that the interaction of carbonyl ligands with electrophiles facilitates the coupling with alkylidyne ligands (lower pathway in Scheme I).[4,5] Photogenerated ketenyl species may be trapped by nucleophiles[6] as well as by electrophiles[7] (middle pathway in Scheme I).

In contrast, the coupling of alkylidyne and isocyanide ligands has so far only been observed as an electrophile-induced process (Scheme II). Proton-induced coupling reactions of alkylidyne and isocyanide ligands were first demonstrated by Filippou and co-workers.[8] We subsequently described a similar reaction.[9] Lippard and Filippou established independently that the bond-forming step in the reductive coupling of two isocyanide ligands occurs as an electrophile-induced aminomethylidyne–isocyanide coupling.[10,11] Recently, Filippou was able to isolate a bis(aminomethylidyne)tungsten complex, generated by alkylation of an (aminomethylidyne)(isocyanide)tungsten complex, and to complete coupling of the two aminomethylidyne ligands by addition of a nucleophile.[12] That study clearly shows the role of the electrophile in activating the isocyanide ligand toward the coupling step. Nucleophile-induced or photoinduced coupling reactions of alkylidyne and isocyanide ligands have not yet been described.

In a number of other bond-forming processes isocyanide ligands are better substrates than carbonyl ligands.[13] For example, only isocyanide ligands participate easily in migratory insertion with hydride ligands or in multiple insertions.[13] While these bond-forming processes may be unrelated to those shown in Schemes I and II, it nevertheless appears surprising that the ability of isocyanide ligands to couple with alkylidyne ligands should be so much less versatile than that of carbonyl ligands. We have recently presented a simple qualitative molecular orbital model to rationalize the behavior of different terminal π-bonded ligands in coupling reactions.[1] It was argued that, in systems with six metal–ligand π electrons, coupling reactions of alkylidyne ligands with π-acceptor ligands become more facile with increasing π bonding between the metal and the ligands (B and C). According to this model, carbonyl ligands are more prone than isocyanide ligands



to undergo coupling with alkylidyne ligands. An especially good situation for coupling is created when both ligands have alkylidyne character.[14] Carbonyl and isocyanide ligands assume alkylidyne character (D and E) after ad-



dition of electrophiles to the oxygen and nitrogen atoms, respectively. Since isocyanide ligands[15] are significantly more nucleophilic than carbonyl ligands,[16] it is understandable that isocyanide ligands undergo electrophile-induced coupling with alkylidyne ligands more easily than carbonyl ligands. However, in nucleophile-induced processes the lower ability of isocyanide ligands to undergo coupling should remain apparent. Experiments to test this situation are described in this work.

Results

We investigated the reaction of the alkylidynetungsten complexes $W(CPh)X(CNCMe_3)_2(CO)_2$ (**1**: **a**, X = Cl; **b**, X = I) and $W(CPh)Cl(CNCMe_3)(CO)(PMe_3)_2$ (**2**) under typical conditions for nucleophile-induced coupling (eqs 3, 5, and 6).[1] These complexes simultaneously contain carbonyl and isocyanide ligands, therefore allowing a direct comparison of the relative reactivity of these ligands. The isocyanide complex **1a** was prepared by substitution of the two pyridine ligands in complex **3** with *tert*-butyl isocyanide (eq 1), in analogy to the synthesis of $W(CPh)Br(CNCMe_3)_2(CO)_2$.[17] Complex **1b**[18] was prepared in a modification of a literature procedure by reaction of **3**[19] with NaI in THF followed by treatment with $CNCMe_3$ in CH_2Cl_2 (eq 2).

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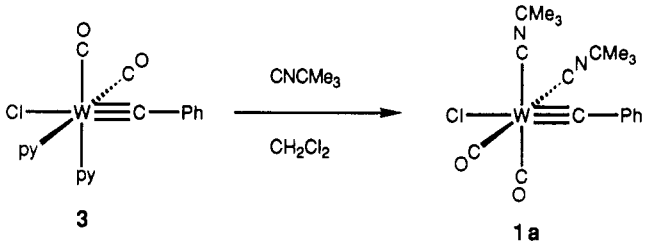
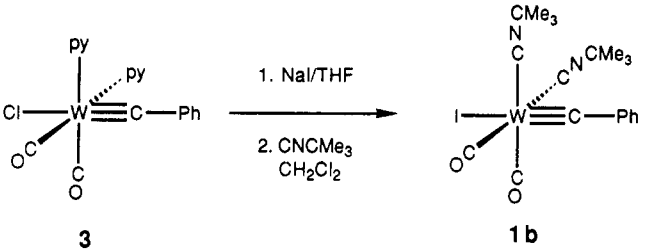
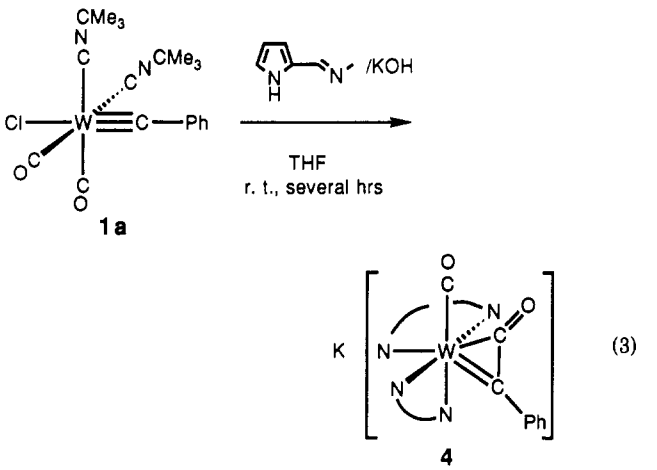


3 1a (1)



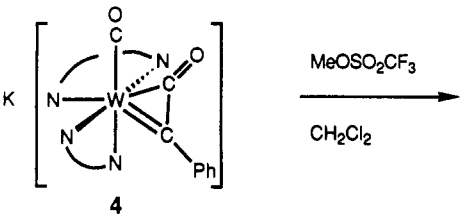
3 1b (2)

When a solution of complex **1a** and pyrrole-2-carboxaldehyde methylimine is stirred in THF, in the presence of KOH, the color of the solution changes from yellow to brown (eq 3). The two ν(CO) stretches at 2015 and 1958



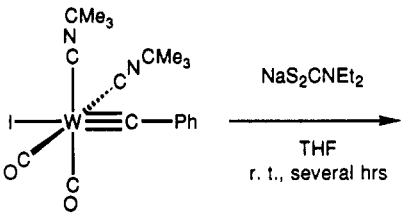
1a 4 (3)

cm^{-1} for the starting material gradually disappear while a strong absorption at 1824 cm^{-1} and a weak absorption at 1655 cm^{-1} gain in intensity. In addition, two new absorptions are seen at 1604 and 1584 cm^{-1} for the coordinated pyrrole-2-carboxaldehyde methyliminate ligands. These absorptions show that the product is complex **4**, which was previously obtained by reaction of **3** with pyrrole-2-carboxaldehyde methylimine under essentially the same conditions.[20] The conversion of **1a** to **4** was at least 90%, as indicated by IR. An absorption at 2133 cm^{-1} was observed for the liberated *tert*-butyl isocyanide.[21] To confirm the nature of **4**, the solvent was removed in vacuo and the residue redissolved in CH_2Cl_2 and treated with $MeOSO_2CF_3$ (eq 4). It had previously been shown that methylation of **4** affords the methoxyacetylene complex **5**.[20] Complex **5** was indeed isolated in 15% yield and characterized by IR and ^1H NMR spectroscopy. Thus, the reaction of **1a** with pyrrole-2-carboxaldehyde methylimine/KOH leads to substitution of both isocyanide ligands and alkylidyne–carbonyl coupling. The reaction of complex **1b** with sodium diethyldithiocarbamate leads to



4 5 (4)

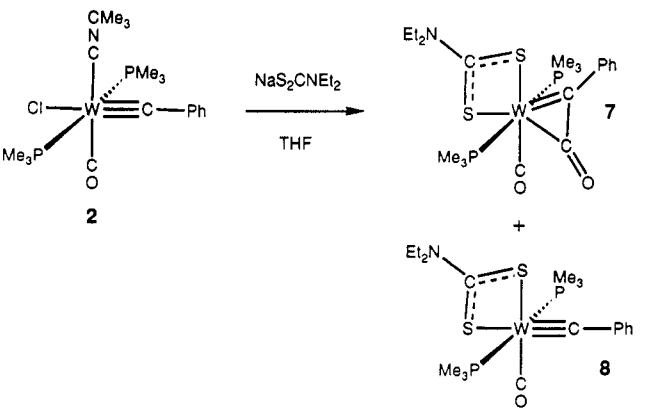
a mixture of products (eq 5). A strong absorption at 1824



1b 6 + unidentified products (5)

cm^{-1} and a weak absorption at 1683 cm^{-1} indicate the formation of the ketenyl complex **6** and account for about 50% of the carbonyl-containing products. Thus, in this reaction substitution of the isocyanide ligands and alkylidyne–carbonyl coupling is also the major reaction pathway. Complex **6** was not successfully separated from the byproducts. Complex **6** was previously obtained by reaction of complex **3** with sodium diethyldithiocarbamate.[22]

The second type of complex investigated is **2**. The reaction of **2** with sodium diethyldithiocarbamate in THF solution proceeds only sluggishly, resulting in the formation of a mixture of products (eq 6). The IR spectrum of the



2 7 + 8 (6)

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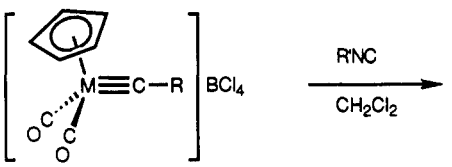
reaction solution exhibits two prominent peaks in the metal carbonyl region at 1883 cm^{-1} and at 1859 cm^{-1}, which are assigned to $[W(PhCCO)(S_2CNEt_2)(CO)(PMe_3)_2]$ (7) and $[W(CPh)(S_2CNEt_2)(CO)(PMe_3)_2]$ (8).[20] The ketenyl complex 7 was successfully separated from the reaction mixture by chromatography on silica gel and isolated in 15% yield. Complex 7 has previously been obtained by reaction of $W(CPh)Cl(CO)_2(PMe_3)_2$ with NaS_2CNEt_2 and complex 8 by reaction of $W(CPh)Cl(CO)(PMe_3)_3$ with NaS_2CNEt_2.[23] It has also been demonstrated that in complex 2 alkylidyne–isocyanide coupling may be induced by the addition of HCl.[9]

Discussion

The reactions of the (alkylidyne)(isocyanide)carbonyltungsten complexes 1 and 2 with anionic chelate ligands (eqs 3, 5, and 6) lead to the substitution of isocyanide ligands and alkylidyne–carbonyl coupling in all three investigated cases. In one case (eq 3) this was essentially the exclusive outcome. Given the fact that we were unable to characterize all of the products in the reaction mixtures, we cannot exclude the possibility that alkylidyne–isocyanide coupling reactions accompanied the substitution of the isocyanide ligands. Nevertheless, the results establish that the isocyanide ligands in complexes 1 and 2 are less able than the carbonyl ligands to undergo nucleophile-induced coupling with the alkylidyne ligand.

Even though no evidence for nucleophile-induced alkylidyne–isocyanide coupling in the reactions shown in eqs 3, 5, and 6 were discovered, it is of interest to consider what the outcome of such steps might have been. The potential products of alkylidyne–isocyanide ligands may be described as iminoketenyl ligands in analogy to the products of alkylidyne–carbonyl coupling. Such ligands have previously been obtained by Fischer through the direct addition of isocyanides to the alkylidyne ligands in the cationic complexes $[M(CR)(\eta^5\text{-}C_5H_5)(CO)_2][BF_4]$ (9) (eq 7).[24]



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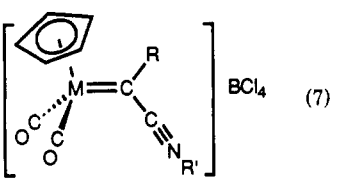
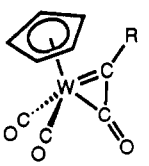


10 (7)

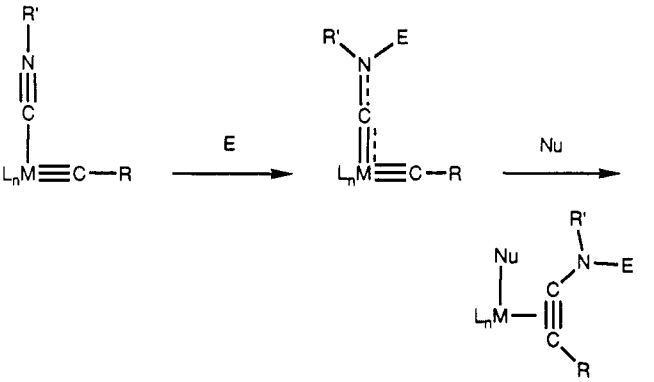
M = Mn, Re; R = alkyl, aryl; R'= Me, *t*-Bu

The isocyanide adducts 10 of complexes 9 are analogs of the η^2-ketenyl tungsten complexes 11, but the bonding of

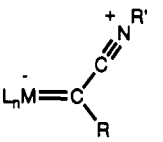


11

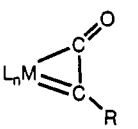
Scheme II



the iminoketenyl ligand (F) is obviously very different from that of the ketenyl ligand (G). The ketenyl ligand is

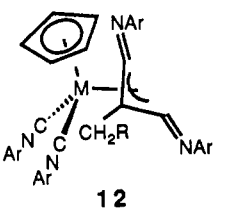


F



G

interacting with the metal center via two carbon atoms (η^2-R*C*C*O*), while the iminoketenyl ligand bonds to the metal center only via one carbon atom (η^1-R*C*C*N*R′). Both ligands, however, if considered as monoanions, are donating four electrons to the metal center. The difference between the two bonding modes probably originates in the π-acceptor ability of the ligands. The ketenyl ligand in 11 is a reasonable π acceptor,[25] while the iminoketenyl ligand in 10 apparently exhibits no π-acceptor properties. Due to the particular bonding the iminoketenyl ligands in complexes 10 exhibit IR absorptions in the CN triple-bond region at about 2220 cm^{-1}. If the iminoketenyl ligand in complexes 10 can be considered as typical for potential alkylidyne–isocyanide coupling products, one should expect prominent IR absorptions in the 2150–2250-cm^{-1} region. No significant absorptions in this region, however, were observed. Another relevant report describes the formation of $M(\eta^5\text{-}C_5H_5)\{Me_3CCH_2C(CNAr)_2\}(CNAr)_2$ (12:



12

M = Mo, W; Ar = C_6H_3-2,6-Me_2) from the alkylidyne complexes $M(CCH_2CMe_3)\eta^5\text{-}C_5H_5)[P(OMe)_3]_2$ and CNAr.[26] On the basis of NMR studies Green postulated that carbon–carbon bond formation in this system occurs by direct addition of isocyanide to the metal–carbon triple bond, i.e. not by coupling of the alkylidyne ligand with coordinated isocyanide.

In conclusion, the present work supports the expectation[1] that the coupling of alkylidyne and isocyanide ligands in Fischer-type metal alkylidyne complexes is not easily induced by nucleophiles. If it is correct that increasing

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π bonding between the metal and the coupling partner CX (B and C) is favoring the coupling process, then one should be able to improve the conditions for coupling by increasing the electron density of the metal center or by using isocyanide ligands with stronger π-acceptor properties.

Experimental Section

Standard inert-atmosphere techniques were used in the execution of the experiments. The solvents methylene chloride (CaH_2), tetrahydrofuran (Na/benzophenone), and hexane (CaH_2) were dried and distilled prior to use. $[W(CPh)(Cl)(CO)_2py_2]$ (**3**)[19] and $[W(CPh)Cl(CNCMe_3)(CO)(PMe_3)_2]$ (**2**)[27] was prepared as previously described. NaS_2CNEt_2 was dried at 110 °C under vacuum for 6 h prior to use. *N*-Methylpyrrole-2-carboxaldimine[28] was prepared as described in the literature. The NMR spectra were measured at a magnetic field strength of 5.87 or 7.05 T (250 or 300 MHz for ^1H NMR) in $CDCl_3$ at room temperature unless otherwise noted; solvent peaks were used as internal reference, and the data are reported in δ relative to TMS, based on residual solvent peaks. The elemental analysis was performed by Schwarzkopf Microanalytical Laboratory.

$[W(CPh)(Cl)(CO)_2(CNCMe_3)_2]$ (1a). A solution of complex **3** (1.027 g, 1.97 mmol) and *tert*-butyl isocyanide (0.488 mL, 4.32 mmol) in CH_2Cl_2 (75 mL) is stirred for 24 h at room temperature. During this time the solution turns red. The solvent is removed in vacuo. The product is purified by filtration through a plug of silica gel at −70 °C, using a 2:1 mixture of Et_2O/CH_2Cl_2 as the solvent. A yellow solution is collected and evaporated to dryness. Crystallization affords amber needles (0.417 g, 40%): ^1H NMR δ 7.36–7.24 (m, 5 H, C_6H_5), 1.63 (s, 18 H, $C(CH_3)_3$; IR (CH_2Cl_2, cm^{-1}) 2184 (m, CN), 2167 (m, CN), 2015 (s, CO), 1958 (s, CO). Anal. Calcd for $C_{21}H_{23}ClN_2O_2W$ (mol wt 530.71): C, 42.96; H, 4.38. Found: C, 42.88; H, 4.28.

$[W(CPh)(I)(CO)_2(CNCMe_3)_2]$ (1b).[18] A solution of complex **3** (0.122 g, 0.23 mmol) and NaI (0.907 g, 6.05 mmol) in THF (10 mL) is stirred at room temperature for 12 h. The solvent is removed in vacuo and the residue redissolved in CH_2Cl_2. The resulting solution is filtered and concentrated to a small volume. Addition of hexane results in the formation of dark orange needles of $[W(CPh)I(CO)_2(py)_2]$ (1.064 g, 99%): IR (CH_2Cl_2, cm^{-1}) 1989 (s, CO), 1904 (s, CO).

A larger sample of $[W(CPh)I(CO)_2(py)_2]$ (4.231 g, 6.89 mmol) is dissolved in CH_2Cl_2 and *tert*-butyl isocyanide (1.604 mL, 14.2 mmol) is added. The solution is heated to reflux for 3 h. The solvent is removed. The residue is redissolved in a 2:1 mixture of Et_2O/CH_2Cl_2 and filtered through a short plug of silica gel at −78 °C. Excess solvent is used to remove all product from the silica gel layer. The solvent is removed from the collected filtrate. Recrystallization from CH_2Cl_2/Et_2O/hexane affords yellow needles (4.01 g, 99%). Complex **1b** is more easily obtained in pure form than complex **1a**. IR (CH_2Cl_2, cm^{-1}): 2183 (m, CN), 2166 (m, CN), 2014 (s, CO), 1957 (s, CO). The IR absorptions are in good agreement with those reported in the literature.[18]

Reaction of 1a with Pyrrole-2-carboxaldehyde Methylimine/KOH. A solution of **1a** (0.150 g, 0.25 mmol) and pyrrole-2-carboxaldehyde methylimine (0.055 g, 0.50 mmol) in THF (7 mL) is stirred at room temperature over a crushed KOH pellet. The solution turns rapidly dark, but the reaction takes about 5 h to go to completion. After 4 h the IR spectrum shows, in addition to residual absorptions of the starting materials, a peak at 2133 (m) cm^{-1} for free *tert*-butyl isocyanide and absorptions at 1824 (s), 1655 (vw), 1604 (m), and 1584 (m) cm^{-1}, which are characteristic for the anionic ketenyl complex $[W(PhCCO)(C_6H_7N_2)_2(CO)]^-$ (**4**). The reported literature values (NEt_4 salt) are 1839, 1665, 1605, and 1582 cm^{-1}.[20]

Characterization of 4 by Transformation into $[W(C_6H_7N_2)_2(PhCCOMe)(CO)]$ (5). A solution of **4** (0.097 g, 0.18 mmol) and pyrrole-2-carboxaldehyde methylimine (0.036 g, 0.16 mmol) is stirred over a crushed KOH pellet. After 20 h at room temperature the solution is filtered, the solvent is removed in vacuo, and the residue is washed with hexane. The solid is taken up in cold (0 °C) CH_2Cl_2, and $MeOSO_2CF_3$ (0.021 mL, 0.183 mmol) is added. The mixture is warmed to room temperature, and the solvent is removed in vacuo. The residue is extracted with CH_2Cl_2/hexane (2:1). The resulting solution is filtered through a plug of silica gel at −78 °C, using an additional amount of the same solvent mixture to elute the product. The solvent of the combined eluates is removed in vacuo. Recrystallization of the product from CH_2Cl_2 affords green crystals (0.017 g, 15%): ^1H NMR δ 8.1 (s, 1 H), 7.78 (s, 1 H), 7.49 (m, 1 H), 7.42–7.20 (m, 5 H), 7.05 (m, 2 H), 6.80 (m, 1 H), 6.51 (m, 1 H), 6.38 (m, 1 H), 6.05 (m, 1 H), 5.85 (s, 1 H), 4.25 (s, 3 H), 3.23 (s, 3 H), 3.04 (s, br, 3 H); IR (CH_2Cl_2, cm^{-1}) 1925 (s, CO), 1686 (w, CCO), 1604 (m, C=N), 1586 (m, C=N). These spectroscopic data are essentially identical with those reported in the literature.[20]

Reaction of 1b with NaS_2CNEt_2. Sodium diethyldithiocarbamate (0.077 g, 0.45 mmol) is added to a solution of **1b** (0.131 g, 0.22 mmol) in THF (10 mL). The solution is stirred for 24 h, during which time the color gradually turns brown. The IR spectrum indicates the formation of a mixture of products. The strongest absorption in the metal carbonyl region at 1824 cm^{-1} is accompanied by a weak absorption at 1683 cm^{-1}. These absorptions are indicative of the formation of $Na[W(PhCCO)(S_2CNEt_2)_2(CO)]$ (**6**).[22] A weak peak at 2133 cm^{-1} shows the presence of free *tert*-butyl isocyanide. After completion of the reaction the following additional peaks are observed: 2126 (w), 1919 (s), and 1882 (s) cm^{-1}. The products were not separated successfully.

Reaction of 2 with NaS_2CNEt_2. A solution of **2** (1.43 g, 2.5 mmol) and sodium diethyldithiocarbamate (0.465 g, 2.7 mmol) in THF (75 mL) is stirred for 4 h at 40 °C and an additional 14 h at room temperature. During this time the color changes from yellow to green-brown. The IR spectrum indicates the formation of a mixture of products. The two major peaks at 1883 cm^{-1} and at 1859 cm^{-1} are assigned to $[W(PhCCO)(S_2CNEt_2)(CO)(PMe_3)_2]$ (**6**)[18] and $[W(CPh)(S_2CNEt_2)(CO)(PMe_3)_2]$ (**9**).[18] A third, weaker absorption in the metal carbonyl region at 1919 cm^{-1} could not be assigned. Complex **6** was successfully separated by column chromatography (silica gel/ethyl acetate, −30 °C) and obtained as a purple solid (0.235 g, 15.3%): ^1H NMR δ 7.74 (d, 2 H, C_6H_5), 7.39 (t, 2 H, C_6H_5), 7.28 (t, 1 H, C_6H_5), 3.80 (q, 2 H, NCH_2), 3.66 (q, 2 H, NCH_2), 1.29 (t, 18 H, PMe_3), 1.34–1.20 (m, 6 H, CH_3); ^{13}C NMR δ 223.6 (t, CO), 206.6, 206.0 (CS_2 and PhCCO), 204.6 (t, PhCCO), 149.8 (ipso C_6H_5), 128.9, 126.8, 125.5 (C_6H_5), 44.44, 44.1 (NCH_2CH_3), 16.0 (t, $P(CH_3)_3$), 12.6, 12.3 (NCH_2CH_3); IR (CH_2Cl_2, cm^{-1}) 1873 (s, CO), 1685 (w, CCO). These data are essentially identical with those found for **6** obtained by reaction of $W(CPh)Cl(CO)_2(PMe_3)_2$ with NaS_2CNEt_2.[23]

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