sociated with the metal d orbitals as the symmetry of the complexes is progressively lowered.[14] For the metallocene complexes, transitions from both the a and 1e orbitals to 2e(dσ*) give rise to the three observed bands listed in Table II.[12] The splitting between the two lowest energy bands in the metallocene spectra arises in part from the differences in energy of the a and 1e levels. The energy separation of bands I and II in the spectra listed in Table I probably has a similar origin; in any case, it is not attributable solely to a splitting of 2e(dσ*), although such a splitting may contribute to the increased separation of the bands as the ligand field strengths of X and L diverge.

The proposed electronic structure for the complexes $Cp^*(PMe_3)_2MX$, in which the dσ* orbitals possess considerable σ-antibonding character with respect to the $M-PMe_3$ and M-X bonds, is in accord with the observed photochemistry for $Cp^*(PMe_3)_2RuX$ (X = H, CH_3, CH_2CMe_3, CH_2SiMe_3), i.e. activation of sp^2 and sp^3 C-H bonds under broad-band UV irradiation ($\lambda_{ex} > 300$ nm). Promotion of an electron to a dσ* orbital would reduce the corresponding M-L or M-X bond strength and lead to photolability of PMe_3 or homolysis of the M-X bond, at least when X is a one-electron σ donor (e.g. hydride or alkyl); see eq 6.

Finally, we note that the use of $Cp^*(PMe_3)_2MX$ has allowed variation of the metal-ligand environment over a range not usually encompassed in spectroscopic studies of organometallic species. In turn, this has allowed the assignment of the electronic structure of these complexes despite their low symmetry. The analogy to the metallocene spectra is both striking and useful as a tool for assigning spectroscopic features in these complexes. The electronic structure proposed can be correlated to the observed photochemistry of these complexes.

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Synthesis of Carbyne Complexes of Chromium, Molybdenum, and Tungsten by Formal Oxide Abstraction from Acyl Ligands

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Reaction of the acyl metal complexes $[NMe_4][M(C(O)R)(CO)_5]$ (R = C_6H_5, M = Cr, Mo, W; R = CH_3, M = W) with the Lewis acids $COCl_2$, $C_2O_2Cl_2$, $C_2O_2Br_2$, and $ClC(O)OCCl_3$ in CH_2Cl_2 at low temperatures (≤-78 °C) and subsequent warming of the solutions (≤0 °C) lead to clean formation of *trans*-halo(carbyne)tetracarbonylmetal complexes, $[M(CR)(X)(CO)_4]$ (X = Cl, Br). The carbyne complexes $[M(CR)X(CO)_4]$ are transformed into stabilized derivatives $[M(CR)X(CO)_2L_2]$ by the addition of donor ligands (L_2 = $(pyridine)_2$ (py), tetramethylethylenediamine (tmeda), bipyridine (bpy)). The complex $[W(CPh)(O_2CCF_3)(CO)_2(tmeda)]$ is prepared in a similar reaction sequence from $[NMe_4][W(C(O)Ph)(CO)_5]$, $(CF_3CO)_2O$, and tmeda. Reaction of $[NMe_4][W(C(O)Ph)(CO)_5]$ with $C_2O_2Br_2$ and 1 equiv of PPh_3 gives $[W(CPh)Br(CO)_3(PPh_3)]$. The bis(pyridine)-substituted complexes $[W(CPh)Cl(CO)_2(py)_2]$ undergo further substitution reactions with PMe_3 and $Ph_2PCH_2CH_2PPh_2$ (dppe) to give $[W(CPh)Cl(CO)_2(PMe_3)_2]$ and $[W(CPh)Cl(CO)_2(dppe)]$.

Introduction

Metal-carbon triple bonds in transition-metal carbyne, or alkylidyne, complexes are well-established functionalities in organometallic chemistry.[1] Tris(alkoxy)metal alkylidyne complexes of tungsten and molybdenum have been shown to be very active acetylene metathesis catalysts,[2] and *trans*-bromotetracarbonyltungsten carbyne complexes are precursors for active acetylene polymerization catalysts.[3] Several stoichiometric reactions of metal carbyne complexes of potential synthetic use have been discovered, such as the formation of ketenyl ligands by carbonyl-carbyne coupling[4] or the incorporation of carbyne ligands into cyclopentadienyl rings,[5] phenols,[6] olefins,[7] acetylenes,[7] and malonic acid derivatives.[8] Metal-carbon triple bonds have also been demonstrated to undergo formal cycloaddition reactions[9] and have been utilized in the systematic build up of transition-metal cluster structures.[10] Nevertheless, the chemistry of transition-metal carbynes is much less investigated than that of the related transition-metal carbene complexes.[11] One of the reasons for this situation is certainly that metal carbynes are less

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Table I. Characteristic ^{13}C NMR Data for Metal Carbyne Complexes 13–27

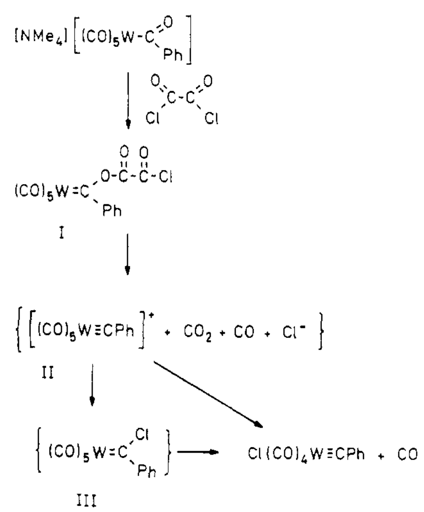
compound	δ(CR)	J_{CW}, Hz
Cr(≡CPh)Br(CO)$_2$(py)$_2$ (**13**)	ref 21	
Cr(≡CPh)Cl(CO)$_2$(tmeda) (**14**)	297.6	
Mo(≡CPh)Br(CO)$_2$(py)$_2$ (**15**)	276.2	
Mo(≡CPh)Cl(CO)$_2$(tmeda) (**16**)	274.3	
W(≡CPh)Cl(CO)$_2$(py)$_2$ (**17**)	262.7	198
W(≡CPh)Br(CO)$_2$(py)$_2$ (**18**)	ref 21	
W(≡CPh)Cl(CO)$_2$(tmeda) (**19**)	262.5	198
W(≡CPh)Br(CO)$_2$(tmeda) (**20**)	262.8	198
W(≡CPh)Cl(CO)$_2$(bpy) (**21**)	265.8	
W(≡CMe)Cl(CO)$_2$(py)$_2$ (**22**)	273.9	198
W(≡CPh)Br(CO)$_3$(PPh$_3$) (**23**)	ref 21	
W(≡CPh)Cl(CO)$_2$(PMe$_3$)$_2$ (**24**)	266.0	194
W(≡CPh)Cl(CO)$_2$(dppe) (**25**)	267.3	
W(≡CMe)Cl(CO)$_2$(dppe) (**26**)	279.3	200
W(≡CPh)(O$_2$CCF$_3$)(CO)$_2$(tmeda) (**27**)	274.1	194

easily accessible. Therefore, the development of general and efficient methods for the preparation of transition-metal carbyne complexes is still an important objective in this area of organometallic chemistry.

Previously, we reported a new metal carbyne complex synthesis based on double β-addition of electrophiles to acetylide ligands.[12] Here we describe in detail a new facile and highly efficient method for the synthesis of mono- and bis-donor ligand-substituted carbyne complexes of chromium, molybdenum, and tungsten. The synthetic procedure consists of direct transformation of the anionic pentacarbonylmetal acyl complexes, $[M(C(O)R)(CO)_5]^-$, into *trans*-halotetracarbonylmetal carbyne complexes, $[M(\equiv CR)X(CO)_4]$, by reaction with carbon-based Lewis acids and subsequent substitution of carbon monoxide by donor ligands. A preliminary account of this work has been published.[13] This reaction was also utilized in the preparation of tris- and tetrakis(trimethylphosphite)-substituted derivatives[14] and in the synthesis of the oxidized tribromometal alkylidyne complexes $[M(\equiv CR)Br_3(dme)]$ (dme = dimethoxyethane).[15] An important aspect of this work is the preparation of derivatives of the tetracarbonylmetal carbyne complexes that exhibit increased thermal stability and at the same time contain coordinatively labile ligands for high reactivity. These properties are combined in some metal carbyne complexes containing simple donor ligands, e.g., in the bis(pyridine)-substituted compounds $[W(\equiv CR)X(CO)_2(py)_2]$. The exploration of the chemistry of these species has already resulted in the isolation of stable tungsten alkene carbyne complexes[16] and in the discovery of reactions leading to incorporation of carbyne ligands into thioformaldehyde ligands.[17]

The synthetic scheme described in this work is based in large part on chemistry previously outlined by Fischer and his group. The most widely used method for carbyne complex synthesis is abstraction of alkoxide from (alkoxycarbene)metal complexes.[1a,18] The requisite (alkoxycarbene)metal complexes are obtained by alkylation of the respective acylmetal complexes.[19] Thus, formal abstraction of oxide, O^{2-}, from acyl ligands represents a more direct route to metal carbyne complexes. Feasibility of this kind of ligand transformation was demonstrated by Fischer in the reaction of $Li[W(C(O)Ph)(CO)_5]$ with phosphorus-based Lewis acids, e.g., Ph_3PBr_2.[20] Fischer also showed that the stability of the *trans*-halotetracarbonyl carbyne complexes of chromium, molybdenum, and tungsten is greatly increased by substitution of one or two carbonyl ligands by donor ligands.[21] The new synthetic scheme described in this work combines the shortness of direct conversion of metal acyl complexes into metal carbyne complexes with the advantages of stabilization of carbyne complexes by donor ligands. Furthermore, with suitable donor ligands, a high degree of coordinative lability, that is reactivity, can be maintained.

Scheme I



Results

Reaction of the anionic acyl pentacarbonylmetal complexes $NMe_4^+[M(C(O)R)(CO)_5]^-$ (**1**, M = Cr, R = C_6H_5; **2**, M = Mo, R = C_6H_5; **3**, M = W, R = C_6H_5; **4**, M = W, R = CH_3) with an equivalent amount or a slight excess of phosgene, $COCl_2$, or oxalyl halide, $C_2O_2X_2$ (X = Cl, Br), in CH_2Cl_2 at low temperatures (**1**–**3**, −78 °C; **4**, −92 °C) and subsequent warming of the solutions (**1** and **3**, −10 °C; **2** and **4**, −40 °C) lead to very clean formation of *trans*-halotetracarbonylmetal carbyne complexes $[M(\equiv CR)X(CO)_4]$ (**5**–**12**).

$$[NMe_4][M(C(O)R)(CO)_5] \xrightarrow[\substack{\le -78 \text{ to } \le -10\ ^\circ C \\ CH_2Cl_2 \\ -NMe_4X,\ -CO_2,\ -2CO \\ X = Cl,\ Br}]{1.\ C_2O_2X_2} M(\equiv CR)X(CO)_4 \quad (1)$$

1: M = Cr, R = C_6H_5
2: M = Mo, R = C_6H_5
3: M = W, R = C_6H_5
4: M = W, R = CH_3

5: M = Cr, R = C_6H_5, X = Cl
6: M = Cr, R = C_6H_5, X = Br
7: M = Mo, R = C_6H_5, X = Cl
8: M = Mo, R = C_6H_5, X = Br
9: M = W, R = C_6H_5, X = Cl
10: M = W, R = C_6H_5, X = Br
11: M = W, R = CH_3, X = Cl
12: M = W, R = CH_3, X = Br

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The reaction is accompanied by the evolution of gas (CO, CO_2) and the formation of a precipitate of NMe_4X (X = Cl, Br). The tetramethylammonium halides can easily be removed by filtration of the recooled (−78 °C) reaction solutions. Isolation of the pure tetracarbonyl carbyne complexes at this stage is demonstrated for [W(≡CPh)-Br(CO)$_4$] and [W(≡CMe)Br(CO)$_4$].

The solutions of the tetracarbonyl metal carbyne complexes **5–12** can be used directly for further reactions as obtained after the initial warming step. Addition of excess nitrogen donor ligands, L, and further warming to room temperature or slightly above (25–40 °C) lead to clean formation of bis-substituted metal carbyne complexes [M-(≡CR)X(CO)$_2$(L)$_2$]. The ligands used in the preparation of the compounds **13–22** (see Table I) are pyridine (py), bipyridine (bpy), and tetramethylethylenediamine (tmeda).

$$\mathrm{M({\equiv}CR)X(CO)_4} \xrightarrow[\substack{CH_2Cl_2 \\ \le -10\ \text{to}\ \le 40\ ^\circ C \\ -2CO}]{L} \underset{\textbf{13–22}\ \text{(Table I)}}{\mathrm{M({\equiv}CR)X(CO)_2(L)_2}} \quad (2)$$

$$L = py,\ ^1/_2(bpy),\ ^1/_2(tmeda)$$

After removal of the solvent excess ligand is washed away with hexane and the products are redissolved in CH_2Cl_2 and filtered for separation from the tetramethylammonium halides. Minor amounts of dark impurities are removed by filtration or chromatography (CH_2Cl_2/pentane) of cooled solutions (−20 °C) over short layers of silica. The pure products **13–22** are obtained in high yields (85–95%) after recrystallization from CH_2Cl_2/pentane. In crystalline form all complexes are stable enough for handling in air and at room temperature; however, long term storage occurs at low temperatures (−10 to 0 °C).

The donor ligand-substituted metal carbyne complexes can also be prepared in a one-pot synthesis starting from the metal hexacarbonyls. In this procedure, as demonstrated for [W(≡CPh)Cl(CO)$_2$(tmeda)] (**19**), the acyl complex Li[W(C(O)Ph)(CO)$_5$] is first generated by reaction of [W(CO)$_6$] with PhLi in ether. After the solvent is changed to THF, Li[W(C(O)Ph)(CO)$_5$] is allowed to react with $COCl_2$ at −78 °C. After warming to 0 °C and addition of excess tmeda, the solution is allowed to warm to room temperature. The disadvantage of this method is the need to separate the product from residual metal hexacarbonyl.

Reactions of the tetracarbonylmetal carbyne complexes with nitrogen donor ligands always give disubstituted derivatives. However, with suitable ligands, monosubstituted derivatives are also accessible.[21] The complex [W(≡CPh)Br(CO)$_3$(PPh$_3$)][21] was obtained in 78% yield from **3** by reaction with oxalyl bromide (−78 to 0 °C), filtration, and addition of only 1 equiv of triphenylphosphine (eq 3).

$$\mathbf{3} \xrightarrow[\substack{2.\ PPh_3,\ 1\ \text{equiv} \\ CH_2Cl_2}]{\substack{1.\ C_2O_2Br_2 \\ -78\ \text{to}\ 0\ ^\circ C}} \mathrm{[(W{\equiv}CPh)Br(CO)_3(PPh_3)]} \quad (3)$$

The pyridine-substituted complexes easily undergo further substitution of the pyridine ligands (eq 4). Reaction of **21** and **22** with bis(diphenylphosphino)ethane (dppe) in CH_2Cl_2 gives the complexes **25** and **26**, [W(≡CR)Cl(CO)$_2$(dppe)] (**25**, R = C_6H_5; **26**, R = CH_3), in 95 and 88% yields, respectively, after recrystallization from dichloromethane/pentane. The complex [W(≡CPh)Cl-(CO)$_2$(PMe$_3$)$_2$] (**24**) is obtained from **21** by reaction with PMe_3 in CH_2Cl_2 and recrystallization from CH_2Cl_2/pentane in 92% yield (eq 4). The pyridine complex used in

$$\mathrm{[W({\equiv}CR)Cl(CO)_2(py)_2]} \xrightarrow[PR_3\,=\,PMe_3,\ ^1/_2(dppe)]{2PR_3} \mathrm{[(W{\equiv}CR)Cl(CO)_2(PR_3)_2]} \quad (4)$$

this preparation need not be isolated in pure form. In a multigram-scale preparation of **24** the bis(pyridine)-substituted complex **17** is prepared in raw form up to the point where excess pyridine is removed by washing with hexane. Then, **17** is redissolved in CH_2Cl_2 for reaction with PMe_3. After removal of the solvent, the residue is washed with hexane for removal of liberated pyridine and dried. The product is extracted with ether and obtained in crystalline form by cooling of the concentrated ether extracts in 82% yield.

Transformation of the acyl ligands into carbyne ligands can also be achieved with other carbon-based Lewis acids. The complexes [Cr(≡CPh)Cl(CO)$_2$(tmeda)] (**14**) and [Mo(≡CPh)Cl(CO)$_2$(tmeda)] (**16**) were prepared by reaction of **1** and **2** with an equivalent amount of ClC(O)OCCl$_3$ at −78 °C in CH_2Cl_2 followed by addition of tmeda at temperatures between −40 and 0 °C and warming to room temperature. The tungsten acyl complex **3** reacts in a similar reaction sequence with trifluoroacetic anhydride to give the *trans*-trifluoroacetato-substituted carbyne complex [W(≡CPh)(O$_2$CCF$_3$)(CO)$_2$(tmeda)] (**27**) in 78% yield.

The reactions leading to the tetracarbonylmetal carbyne complexes are believed to proceed via attack by the respective reagents at the oxygen atom of the acyl ligands to generate intermediates of the type [M[=C(OC(O)Y)-R](CO)$_5$]. Attempts to characterize by low-temperature NMR the initial product of the reactions between [NMe$_4$][WC(O)Ph(CO)$_5$] (**3**) and phosgene, $COCl_2$, as well as oxalyl bromide, BrC(O)COBr, have not been successful. We have, however, observed that the stability of the low-temperature intermediate is increased by substitution of the phenyl group. Thus, the ^{13}C NMR spectrum of the product between [NEt$_4$][W(C(O)C$_6$H$_4$-*p*-OCH$_3$)(CO)$_5$] and oxalyl bromide has been recorded at −80 °C and was found to be fully consistent with the proposed structure [W[=C(OC(O)COBr)C$_6$H$_4$-*p*-OCH$_3$](CO)$_5$]. Most characteristically, the ^{13}C NMR spectrum exhibits a resonance at 300.5 ppm (J_{CW} = 118.4 Hz) which is typical for pentacarbonyltungsten (acyloxy)arylcarbene complexes.[23b] When the temperature is raised to 0 °C, this intermediate decomposes cleanly into the known carbyne complex [W-(≡CC$_6$H$_4$-*p*-OCH$_3$)Br(CO)$_4$].[22]

The nature of the low-temperature intermediates was also probed by their chemical reactivity. Addition of methanol and triethylamine to the product of the reaction between **3** and $COCl_2$ at −78 °C in THF and warming to room temperature lead to formation of [W(=C(OMe)-Ph)(CO)$_5$] (**28**) in 18% yield. This reaction may proceed via the further intermediate [W[=C(OC(O)OCH$_3$)Ph]-(CO)$_5$]. The same intermediate may be involved in the reaction between **3** and methyl chloroformate in the presence of triethylamine from which **28** is isolated in 74% yield. In a similar reaction where the acyl complex **3** was allowed to react at −78 °C first with oxalyl chloride and then with methanol, the methoxycarbene complex **28** is also formed and isolated in 69% yield.

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Discussion

A variety of carbon-based Lewis acids are able to convert the anionic pentacarbonylmetal acyl complexes $[M(C(O)R)(CO)_5]^-$ (M = Cr, Mo, W) into *trans*-halotetracarbonylmetal carbyne complexes (eq 1). The preferred starting materials are the tetramethylammonium salts **1–4**.[19] These are easily prepared in pure form on a large scale, and with these salts the reactions generate only gaseous or insoluble by products. Thus, very pure solutions of the *trans*-halotetracarbonylmetal carbyne complexes can be obtained. A proposed mechanism for the reaction between **3** and oxalyl chloride is shown in Scheme I. Attack at the oxygen atom of the acyl ligand by the Lewis acid is assumed to be the common step for all reagents used. Precedent for this step exists in the formation of (acyloxy)phenylcarbene complexes $[W[{=}C(OC(O)R')Ph](CO)_5]$ from the reaction of **3** with acyl halides.[23] One intermediate of type I was characterized by ^{13}C NMR from the reaction between $NEt_4[(CO)_5W\text{-}C(O)C_6H_4\text{-}4\text{-}OCH_3]$ and BrC(O)COBr. In the formed intermediate I the oxygen atom of the former acyl ligand has become incorporated into a good leaving group, in this case chlorooxalate, $[O_2CCOCl]^-$ (Scheme I). When the temperature is raised, intermediate I presumably dissociates into the labile cationic carbyne complex $[(CO)_5M{\equiv}CPh]^+$ (II) and the anionic leaving group $[OC(O)COCl]^-$, which itself is unstable and decomposes under liberation of chloride ion. The liberated chloride reacts with the cationic metal carbyne complex II under loss of a carbon monoxide ligand to give the neutral *trans*-halotetracarbonylmetal carbyne complex. This may occur either directly or via the pentacarbonyltungsten chlorocarbene complex III. Pentacarbonylmetal halocarbene complexes are also proposed as intermediates in the reaction of pentacarbonylmetal alkoxycarbene complexes with boron trihalides, the original metal carbyne complex synthesis by Fischer.[24]

The low temperatures for the addition of the acylating agents are chosen to assure sufficient stability of intermediates of type I during the time of reagent addition. If the temperatures are higher, undesirable side reactions can take place. For example, when $COCl_2$ is added to a methylene chloride solution of **3** at −20 °C, the known[25] compound $[trans\text{-}(CO)_5WC(R){=}O{\rightarrow}W{\equiv}CPh(CO)_4]$ (**29**) forms. In **29** the pentacarbonyltungsten benzoyl anion occupies the coordination site trans to the carbyne ligand. Formation of **29** likely occurs by decomposition of $[W[{=}C(Ph)OC(O)Cl](CO)_5]$ in the presence of excess **3**, which acts as a stronger nucleophile toward tungsten than chloride. **29** was previously prepared by reaction of the hydroxycarbene complex $[W({=}C(Ph)OH)(CO)_5]$ with dicyclohexylcarbodiimide.[25]

The nature of intermediates of type I is also indicated by their reactions with methanol to give pentacarbonylmetal methoxycarbene complexes. These reactions are analogous to previously reported transformations of pentacarbonylmetal (acyloxy)carbene complexes into corresponding alkoxy- or phenoxycarbene complexes by reaction with alcohols.[23a,26] In these reactions the good leaving groups $[OC(O)R']^-$ are replaced by methoxide.

The reaction sequence of Scheme I corresponds overall to the removal of oxide from the acyl ligand via the initial replacement of O^{2-} by Cl^-. In that view it belongs to a fairly large family of halogenations of organic and organometallic carbonyl functionalities effected by acid halides. Scheme I, of course, also applies in modified form to the transformation of acyl complex **3** into *trans*-halotetracarbonylmetal carbyne complexes by phosphorus-based Lewis acids[20] or to the transformation of the carboxamido complex $Li[W(C(O)NEt_2)(CO)_5]$ into the aminocarbyne complex $[W({\equiv}CNEt_2)Cl(CO)_4]$ by thionyl chloride.[27] Monosubstituted carboxamido ligands react with phosgene in the presence of base to give isocyanide ligands.[28] Reactions of organic primary formamides with phosgene or diphosgene and base result in isocyanides.[29] Secondary formamides react with phosgene, oxalyl halides, and other acid halides to give formamidimium chlorides.[30] Carboxylate groups are transformed into acyl halide groups by the same reagents.[31]

In the formation of donor-substituted metal carbyne complexes nitrogen-based ligands are preferred, because the bis-substituted products are formed essentially quantitatively and the nitrogenous ligands can generally be subjected to further substitution reactions. Compared to the compounds $[M({\equiv}CR)X(CO)_4]$ the complexes $[M({\equiv}CR)X(CO)_2L_2]$ possess improved thermal stability and at the same time retain a large degree of reactivity. Formation of the bis(nitrogen)-donor-substituted complexes is remarkably insensitive toward prior decomposition of the *trans*-halotetracarbonylmetal carbyne complexes. For example, when $[W({\equiv}CPh)Cl(CO)_4]$ is prepared from **3** and phosgene, excess phosgene, which may have been added inadvertently, can be removed by reducing the volume of the reaction solution, if necessary, to dryness. This procedure usually leads to complete decomposition of the tetracarbonyl carbyne complex **9**; however, redissolution of the residue in CH_2Cl_2 and addition of pyridine still results in high yields of the bis(pyridine)-substituted complex **17**. The decomposition products apparently still contain intact halo(carbyne)dicarbonylmetal entities. Fischer has previously shown that the initial decomposition products of *trans*-halo(carbyne)tetracarbonylmetal carbyne complexes are halo-bridged dinuclear compounds of the type $[M({\equiv}CR)X(CO)_3]_2$.[32]

The dppe-substituted complex $[W({\equiv}CPh)Cl(CO)_2(dppe)]$ can be prepared by direct addition of dppe to a CH_2Cl_2 solution of $[W({\equiv}CPh)Cl(CO)_4]$; however, a cleaner product is obtained by the indirect synthesis via $[W({\equiv}Ph)Cl(CO)_2(py)_2]$. In the synthesis of bis(trimethylphosphine)-substituted complexes it is essential to proceed via bis(nitrogen)-donor-substituted compounds, since trimethylphosphine is known to form ylides by attack at the electrophilic carbyne carbon in tetracarbonylmetal carbyne complexes.[21] In the bis-donor-substituted systems $[M({\equiv}CR)X(CO)_2L_2]$ the polarity of the carbyne carbon is reversed. Therefore, attack by PMe_3 only occurs at the metal center. In contrast to the substitution reactions with nitrogen donor ligands, which always give bissubstituted derivatives, reactions with some phosphine ligands also give monosubstituted complexes $[M({\equiv}CR)X(CO)_3L]$.[21] The complex $[W({\equiv}CPh)Br(CO)_3(PPh_3)]$[21] is conveniently

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prepared by addition of 1 equiv of PPh_3 to a solution of [W(≡CPh)Br(CO)$_4$].

Experimental Section

Standard inert-atmosphere techniques were used in the execution of the experiments. The solvents CH_2Cl_2 (P_4O_{10}), tetrahydrofuran, and diethyl ether (Na/benzophenone) were dried and distilled prior to use. The acylmetal complexes NMe_4[M(C(O)R)(CO)$_5$] were prepared as described in the literature.[19] Reagents were used as obtained from commercial sources. The NMR spectra ($CDCl_3$ solution) were recorded on a Bruker WM250 spectrometer at −20 °C, unless otherwise noted, and the IR spectra (CH_2Cl_2 solution) on a Digilab FT-20 spectrometer. Elemental analyses were performed by Schwarzkopf Analytical Laboratory and by Galbraith Analytical Laboratory.

[W(CPh)Br(CO)$_4$] (10).[18] A solution of 3 (5.032 g, 10 mmol) in CH_2Cl_2 (125 mL) is cooled to −78 °C, whereby a fine precipitate forms. Then a cold solution (−78 °C) of oxalyl bromide (0.95 mL, 10.10 mmol) in CH_2Cl_2 (30 mL) is added to the well stirred suspension. The reaction mixture is warmed in an ice bath just until the color of the solution changes to bright yellow (−20 to −10 °C) and then immediately cooled back to −78 °C. The cold solution is then filtered through a dry-ice-jacketed frit with a 2-cm layer of cellulose or Celite on it. The flask is placed into a water/ice bath and the solvent removed in vacuo to give a yellow solid. The product is purified by chromatography on silica gel at −30 °C. The column (3 cm × 30 cm) is prepared with pentane. The product is transferred onto the column as a suspension in pentane and washed into the column with pentane (100 mL). The product is eluted with pentane/CH_2Cl_2 (5:2) (300 mL) and collected in a cold (−78 °C) flask. Removal of the solvent gives a pale yellow microcrystalline powder (4.0 g, 86%).

[W(CMe)Br(CO)$_4$] (12).[18] A solution of 4 (2.97 g, 6.73 mmol) in CH_2Cl_2 (75 mL) is cooled to −95 °C (CH_2Cl_2/liquid N_2), and a cold (−95 °C) solution of oxalyl bromide (0.67 mL, 7.2 mmol) is added. The deep orange-brown solution is warmed to −78 °C and stirred at that temperature for 10 min. The cold solution is filtered through a dry-ice-cooled frit packed with a 2-cm layer of cellulose and collected in a cold flask. The solution is warmed to 0 °C during which time the color changes to orange-yellow. At this point the reaction vessel is shielded from direct light as the product is photosensitive. The solvent is removed at 0 °C to give a yellow solid. The product is chromatographed on silica gel (3 cm × 15 cm). The eluant is pentane/CH_2Cl_2 (5:2). The product is colorless so the chromatography is followed by IR. The first 200 mL of eluant contains a side product. The product is then eluted with 600 mL of the solvent mixture and collected in a cold (−78 °C) flask. Removal of the solvent at 0 °C gives a colorless solid (1.92 g, 71%).

[Cr(CPh)Br(CO)$_2$(py)$_2$] (13).[21] A solution of 1 (0.743 g, 2.0 mmol) in CH_2Cl_2 (75 mL) is cooled to −78 °C, and a cold (−78 °C) solution of oxalyl bromide (0.19 mL, 2.04 mmol) in CH_2Cl_2 (15 mL) is added. The deep orange solution is warmed in an ice bath just until a bright yellow color develops and then recooled to −78 °C. The cold solution is filtered through a layer of cellulose (2 cm) on a fitted disk. After addition of 1 mL of freshly distilled pyridine the temperature is raised to 0 °C. The solution is stirred at this temperature until the reaction is complete (~1 h). The volume of the resulting red-orange solution is reduced to approximately 5 mL, and the product is precipitated by the addition of 30 mL of pentane as a red oil which subsequently solidifies. After the supernatant is decanted off, the solid is redissolved (at 0 °C) in a small amount of CH_2Cl_2 and precipitated again with pentane as a red-orange oil which solidified as a crystalline mass (0.80 g, 92%).

[Cr(CPh)Cl(CO)$_2$(tmeda)] (14). A solution of 1 (1.86 g, 5.0 mmol) in CH_2Cl_2 (100 mL) is cooled to −78 °C. Diphosgene (0.61 mL, 5.05 mmol) is added dropwise whereby the color of the solution turns deep red. Upon warming to 0 °C in a ice water bath, a bright yellow solution forms. Then tmeda (4 mL, 26 mmol) is added and the temperature raised to 25 °C. After the reaction is completed (1 h), the solvent is removed. The solid is washed with pentane (2 × 20 mL) and redissolved in THF (25 mL), and the resulting solution is filtered to remove NMe_4Cl. The THF is removed in vacuo and the product recrystallized from CH_2Cl_2/pentane to yield a deep red microcrystalline solid (1.61 g, 93%) (mp 126–128 °C dec): ^{1}H NMR δ 7.46 (br, 2 H, H_o-Ph), 7.30 (br, 3 H, $H_{m,p}$-Ph), 3.09 (s, br, 6 H, CH_3-tmeda), 2.74 (s, br, 6 H, CH_3-tmeda), 2.67 (s, br, 4 H, CH_2-tmeda); $^{13}C\{^1H\}$ NMR δ 297.6 (CPh), 230.9 (CO), 146.5 (C_{ipso}-Ph), 129.1 (C_o-Ph), 128.3 (C_p-Ph), 128.1 (C_m-Ph), 59.6, 56.9 (CH_3-tmeda), 51.3 (CH_2-tmeda); IR 1994 (s), 1912 (s) cm^{-1}. Anal. Calcd for $C_{15}H_{21}N_2O_2ClCr$ (M_r 348.70): C, 51.65; H, 6.07; N, 8.03. Found: C, 51.43; H, 6.34; N, 8.23.

[Mo(CPh)Br(CO)$_2$(py)$_2$] (15). 2 (0.831 g, 2.00 mmol) is dissolved in CH_2Cl_2 (75 mL) at 0 °C. The solution is cooled to −78 °C, and a cold (−78 °C) solution of oxalyl bromide (0.191 mL, 2.04 mmol) in CH_2Cl_2 (10 mL) is added. The reaction flask is placed in an ice water bath. When the deep orange-brown color of the solution turns yellow, freshly distilled pyridine (1 mL, 12 mmol) is added. The solution is stirred at 0 °C until the substitution reaction is complete (~1 h). The solvent is removed at 0 °C and the residue washed with pentane (2 × 20 mL). The product is purified by chromatography on silica gel (3 cm × 5 cm) at −78 °C. A solution of the product in a minimum amount of cold (0 °C) CH_2Cl_2 is brought onto the layer of silica gel/CH_2Cl_2 on dry-ice-jacketed fritted disk. The product is eluted with cold (−78 °C) CH_2Cl_2 (250 mL). The solvent is removed at 0 °C to yield a yellow powder (0.744 g, 78%) (mp 120–125 °C dec): the product is not stable above 0 °C; ^{1}H NMR δ 9.08 (d, 4 H, o-py), 7.74 (t, 2 H, p-py), 7.44 (d, 2 H, o-Ph), 7.30 (m, 7 H, m-py, m, p-Ph); $^{13}C\{^1H\}$ NMR δ 276.2 (*C*Ph), 222.6 (CO), 152.5, 138.0, 124.6 (C_5H_5N), 144.5, 128.5, 128.0 (C_6H_5); IR 2003 (s), 1924 (s) cm^{-1}.

[Mo(CPh)Cl(CO)$_2$(tmeda)] (16). A solution of 2 (0.415 g, 1 mmol) in CH_2Cl_2 (20 mL) is cooled to −78 °C. Diphosgene is added dropwise whereby the color turns dark orange. The temperature is raised in an ice water bath. When the color turns bright yellow, tmeda (2 mL, 13 mmol) is added and the solution is stirred at 0 °C until the reaction is complete (1 h). The solvent is removed from the yellow-orange solution and the residue washed with pentane (2 × 15 mL). The solid is dissolved in cold (0 °C) THF, and the resulting solution is filtered to remove NMe_4Cl. Recrystallization of the product from CH_2Cl_2/pentane gives golden needles (0.375 g, 95%) (mp 161–164 °C dec): ^{1}H NMR δ 7.29 (m, 5 H, Ph), 3.09 (s, br, 6 H, CH_3-tmeda), 2.85 (s, br, 10 H, CH_3, CH_2-tmeda); $^{13}C\{^1H\}$ NMR δ 274.3 (*C*Ph), 223.9 (CO), 145.0 (C_{ipso}-Ph), 128.8 (C_o-Ph), 128.3 (C_p-Ph), 128.2 (C_m-Ph), 60.1, 56.7 (CH_3-tmeda), 51.4 (CH_2-tmeda); IR 1997 (s), 1912 (s) cm^{-1}. Anal. Calcd for $C_{15}H_{21}ClN_2O_2Mo$ (M_r 392.73): C, 45.88; H, 5.39; N, 7.13. Found: C, 46.01; H, 5.74; N, 7.53.

[W(CPh)Cl(CO)$_2$(py)$_2$] (17). 3 (5.032 g, 10 mmol) is first dissolved in CH_2Cl_2 (200 mL). Then, the solution is cooled to −78 °C, whereby a fine precipitate forms. Phosgene ($COCl_2$) is lightly blown over the surface of the well-stirred suspension until a slight excess of phosgene is present. Excess phosgene is recognized by its characteristic IR absorption ($\nu_{C=O}$ = ~1810 cm^{-1}). The dark solution is then warmed to 0 °C whereby the color becomes pale yellow. As rapidly as possible the solvent is removed in vacuo until the IR spectrum of the solution shows no absorption of $COCl_2$. Removal of up to 75% of the original volume of solvent shows no effect on the final yield. After addition of excess pyridine (6.5 mL, 80 mmol) the solution is warmed to room temperature. CO is evolved, and the color becomes orange. Completeness of the reaction is indicated by disappearance of the absorption of [Cl(CO)$_4$W≡CPh] (ν_{CO} = 2130 (w), 2040 (s) cm^{-1}) and the simultaneous appearance of the carbonyl absorptions of the product. The reaction is completed after about 2 h at room temperature. The solvent is then removed in vacuo and the solid residue washed with pentane (2 × 50 mL) to remove residual pyridine. The product is purified by chromatography at −30 to −20 °C on a silica gel column (3 × 8 cm). The product is applied to the column with a 1:1 mixture of CH_2Cl_2/pentane and eluted initially with the same mixture (200 mL). Then the eluting solvent is changed to 2:1 CH_2Cl_2/pentane to remove the rest of the product (300 mL). The product is recrystallized by dissolving the solid in a minimum amount of CH_2Cl_2 and adding pentane until cloudiness begins. On cooling to 0 °C orange-gold plates form. A second and a third crop of product are obtained from the mother liquor by further addition of pentane and cooling; yield 4.86 g (93%) (mp 115 °C dec). From CH_2Cl_2/hexane the product is obtained in large orange crystals: ^{1}H NMR δ 9.12 (d, 4 H, H_o-C_5H_5N), 7.82 (t, 2 H, H_p-

C_5H_5N), 7.32 (m, 9 H, H_m-C_5H_5N and C_6H_5); $^{13}C\{^1H\}$ NMR δ 262.7 (J_{CW} = 198 Hz, CPh), 220.4 (CO), 152.7 (C_o-C_5H_5N), 149.2 (C_{ipso}-C_6H_5), 138.2 (C_p-C_5H_5N), 129.3, 127.9, 127.5 (C_6H_5), 125.0 (C_m-C_5H_5N); IR 1985 (s), 1897 (s) cm^{-1}. Anal. Calcd for $C_{19}H_{15}ClN_2O_2W$ (M_r 522.63): C, 43.67; H, 2.89; N, 5.36. Found: C, 43.86; H, 2.98; N, 5.67.

[W(CPh)Br(CO)$_2$(py)$_2$] (18).[21] 3 (22.0 g, 43.7 mmol) is dissolved in CH_2Cl_2 (400 mL) and cooled to −78 °C. A cold (−78 °C) solution of oxalyl bromide (4.14 mL, 44.1 mmol) in CH_2Cl_2 (40 mL) is added. The dark solution is warmed until the color turns yellow (∼−20 to 0 °C). Then pyridine (10 mL) is added, and the temperature is raised to 40 °C. After complete formation of the product (∼1.5 h) the solvent is removed and the residue washed with pentane (2 × 100 mL). The product is redissolved in CH_2Cl_2 (100 mL) and the resulting solution filtered through cellulose. The solution is reduced in volume (∼50 mL) and transferred to a cold (−30 °C) column of silica gel (4 cm × 15 cm) in pentane. A green side product is first removed with CH_2Cl_2/pentane, 1:1. After the green band is removed, the product is eluted with pure CH_2Cl_2. Removal of the solvent gives a bright orange crystalline solid (23.35 g, 94%).

[W(CPh)Cl(CO)$_2$(tmeda)] (19). A solution of 3 (1.51 g, 3.0 mmol) in THF (100 mL) is cooled to −78 °C, and a slight excess of phosgene is added. The purple solution is warmed to 0 °C. The volume is reduced until excess phosgene is removed (IR). Then tmeda (4 mL, 27 mmol) is added, and the reaction mixture is slowly warmed to 40 °C. When the reaction is complete, the solvent is removed and the solid washed with pentane (2 × 20 mL). The solid is dissolved in THF and filtered to remove NMe_4Cl. The THF is removed, and the product is recrystallized from a minimum amount of CH_2Cl_2 and pentane as orange-yellow needles (1.37 g, 95%) (mp 155 °C dec): ^1H NMR δ 7.26 (m, 5 H, C_6H_5), 3.24 (s, 6 H, CH_3-tmeda), 2.96 (s, 6 H, CH_3-tmeda), 2.94 (s, 2 H, CH_2-tmeda), 2.84 (s, 2 H, CH_2-tmeda); $^{13}C\{^1H\}$ NMR δ 262.5 (CPh, J_{CW} = 198 Hz), 221.1 (CO, J_{CW} = 176 Hz), 149.0 (C_{ipso}-C_6H_5), 129 (C_o-C_6H_5), 128.0 (C_m-C_6H_5), 127.4 (C_p-C_6H_5), 61.0 (CH_2-tmeda), 58.1, 52.1 (CH_3-tmeda); IR 1985 (s), 1892 (s) cm^{-1}. Anal. Calcd for $C_{15}H_{21}ClN_2O_2W$ (M_r 480.64): C, 37.48; H, 4.40; N, 5.83. Found: C, 37.20; H, 4.47; N, 5.85.

Synthesis of 19 from W(CO)$_6$. $W(CO)_6$ (1.00 g, 2.84 mmol) is suspended in Et_2O (50 mL), and phenyllithium is added dropwise. After 30 min the solvent is removed in vacuo. The residue is redissolved in THF (40 mL), and the solution is cooled to −78 °C. Phosgene is lightly blown over the surface of the stirred solution until a slight excess is present. Then the temperature is raised to 0 °C, and about 50% of the solvent is removed in vacuo. After the addition of tmeda (2 mL) the reaction mixture is brought to room temperature and stirred for 2 h. The solution is filtered through a pad of cellulose and the solvent removed in vacuo. The residue is redissolved in CH_2Cl_2 (20 mL) and again filtered through a pad of cellulose. The volume of the solution is reduced to about 5 mL and the product precipitated with pentane to remove $W(CO)_6$. The product is recrystallized from CH_2Cl_2/pentane to yield orange-yellow microcrystals (1.06 g, 77%).

[W(CPh)Br(CO)$_2$(tmeda)] (20). Solutions of 3 (1.006 g, 2.0 mmol in CH_2Cl_2 (20 mL) and of oxalyl bromide (0.19 mL, 2.0 mmol) in CH_2Cl_2 (10 mL) are combined at −78 °C. The dark orange solution is warmed in an ice-water bath. When the color turns yellow, tmeda (2 mL, 13 mmol) is added and the solution is warmed to 40 °C. The product is isolated as described for 19. Yellow-orange needles (1.0 g, 95%) (mp 170–175 °C dec): ^1H NMR δ 7.27 (m, 5 H, C_6H_5), 3.27 (s, 2 H, CH_2-tmeda), 3.24 (s, 6 H, CH_3-tmeda), 3.05 (s, 2 H, CH_2-tmeda), 2.95 (s, 6 H, CH_3-tmeda); $^{13}C\{^1H\}$ NMR δ 262.8 (J_{CW} = 198 Hz, CPh), 221.2 (J_{CW} = 176 Hz, CO), 148.7 (C_{ipso}-C_6H_5), 129.3, 127.9, 127.4 ($C_{o,m,p}$-C_6H_5), 60.9 (CH_3-tmeda), 58.0 (CH_2-tmeda), 52.0 (CH_3-tmeda); IR 1983 (s), 1892 (s) cm^{-1}. Anal. Calcd for $C_{15}H_{21}BrN_2O_2W$ (M_r 525.10): C, 34.31; H, 4.03; N, 5.33. Found: C, 34.61; H, 4.33; N, 5.05.

[W(CPh)Cl(CO)$_2$(bpy)] (21). 3 (1.00 g, 1.94 mmol) is dissolved in CH_2Cl_2 (50 mL) and cooled to −78 °C. A slight excess of $COCl_2$ is added, and the solution is allowed to warm to ∼−5 °C during which time a pale yellow color develops. Then between $^1/_2$ to $^2/_3$ of the solvent is removed in vacuo at 0 °C, 2,2′-bipyridyl (bpy) (0.38 g, 2.33 mmol) is added, and the solution is warmed to 40 °C. During this time the solution turns deep red. After the reaction is completed (IR), the solvent is removed in vacuo. The product is chromatographed on silica gel at −30 °C. The initial eluant is CH_2Cl_2/pentane, 1:1, to remove any excess bpy. The product is eluted with pure CH_2Cl_2 and recrystallized from CH_2Cl_2/Et_2O to give deep red microcrystals (0.97 g, 94%) (mp 212 °C dec). The product can also be purified by simple recrystallization: ^1H NMR δ 9.35 (d, 2 H, $H_{6,6'}$bpy), 8.24 (d, 2 H, $H_{3,3'}$bpy), 8.08 (t, 2 H, $H_{5,5'}$bpy), 7.57 (t, 2 H, $H_{4,4'}$bpy), 7.19 (m, 5 H, phenyl); $^{13}C\{^1H\}$ NMR δ 265.8 (CPh), 222.2 (CO), 155.4 ($C_{2,2'}$bpy), 154.2 ($C_{6,6'}$bpy), 139.4 (C_{ipso}-C_6H_5), 129.6 ($C_{3,3'}$bpy), 127.7 (C_o-C_6H_5), 127.5 ($C_{4,4'}$bpy), 126.5 (C_m-C_6H_5), 122.8 (C_p-C_6H_5); IR 1986 (s), 1899 (s) cm^{-1}. Anal. Calcd for $C_{19}H_{13}ClN_2O_2W$ (M_r 520.63): C, 43.83; H, 2.52; N, 5.38. Calcd for 21·$^1/_2Et_2O$ (solvate) ($C_{21}H_{18}ClO_{2.5}N_2W$): C, 45.23; H, 3.22; N, 5.02. Found: C, 45.21; H, 3.04; N, 5.06.

[W(CMe)Cl(CO)$_2$(py)$_2$] (22). A solution of 4 (0.441 g, 1 mmol) is dissolved in CH_2Cl_2 (200 mL) and cooled to −92 °C (or lower). A stream of phosgene gas is blown over the surface of the solution until a slight excess of phosgene is present. Excess phosgene is recognized by its characteristic IR absorption ($\nu_{C=O}$ = ∼1810 cm^{-1}). The temperature is raised to 0 °C, and enough solvent is evaporated in vacuo (up to $^2/_3$ of volume) to ensure removal of excess phosgene. After addition of distilled pyridine (5 mL) the solution is warmed to room temperature. When the reaction is completed (∼50 min), the solvent is removed and the residue washed with pentane (3 × 5 mL). The dried product is dissolved in THF (10 mL, 0 °C) and filtered to remove NMe_4Cl. The solvent is removed, and the produce is recrystallized from CH_2Cl_2/pentane. Yellow needles are obtained by layering pentane (20 mL) on top of a solution of the product in a small amount of CH_2Cl_2 (∼5 mL) and slow cooling to −5 °C (0.393 g, 85%) (mp 110–115 °C dec). Less pure samples can be chromatographed on silica with CH_2Cl_2/pentane (1:1) as the eluant: ^1H NMR δ 8.97 (d, 4 H, o-py), 7.82 (t, 2 H, p-py), 7.32 (t, 4 H, m-py), 2.41 (s, 3 H, CH_3); $^{13}C\{^1H\}$ NMR δ 273.9 (J_{CW} = 197.5 Hz, CMe), 219.8 (J_{CW} = 177.8 Hz, CO), 152.6, 138.0, 124.8 (py), 35.4 (CH_3); IR 1982 (s), 1889 (s) cm^{-1}. Anal. Calcd for $C_{14}H_{13}ClN_2O_2W$ (M_r 460.57): C, 36.50; H, 2.82; N, 6.08. Found: C, 36.15; H, 3.02; N, 6.08.

[W(CPh)Br(CO)$_3$(PPh$_3$)] (23).[21] A solution of 3 (10.06 g, 20.0 mmol) in CH_2Cl_2 (30 mL) is cooled to −78 °C, and a cold (−78 °C) solution of oxalyl bromide (1.89 mL, 20.2 mmol) in CH_2Cl_2 (50 mL) is added. After the solution was stirred for about 5 min, the reaction flask is placed in an ice-water bath. When the color lightens to yellow, PPh_3 (5.25 g, 20.0 mmol) is added and the solution is allowed to warm to room temperature. The reaction is monitored by IR (ν_{CO} = 2078 (m), 1998 (s) cm^{-1});[21] it takes approximately 3.5 h to completion. Then the temperature is lowered to −78 °C, and the solution is filtered through a pad of cellulose to remove NMe_4Br. The solvent is removed in vacuo and the product chromatographed on silica gel at −20 °C (3 cm × 10 cm) eluting with CH_2Cl_2/pentane, 1:1. A yellow band is collected into a cooled flask (−78 °C). After removal of the solvent a bright yellow powder is obtained (10.85 g, 78%).

[W(CPh)Cl(CO)$_2$(PMe$_3$)$_2$] (24). 17 (2.61 g, 5.0 mmol) is dissolved in THF (100 mL), and PMe_3 (1.21 mL, 11.1 mmol) is added. The temperature is raised to 50 °C until the reaction is complete (1 h). During this time the color changes from orange to yellow. The solvent is removed in vacuo and the solid washed with cold (0 °C) pentane (2 × 20 mL). The product is recrystallized from CH_2Cl_2/pentane to give orange-yellow crystals (2.37 g, 92%) (mp 132–135 °C dec): ^1H NMR δ 7.25 (m, 5 H, Ph), 1.69 (d, 18 H, PMe_3, $^2J_{HP}$ = 7.7 Hz); $^{13}C\{^1H\}$ NMR δ 266.0 (J_{CW} = 194 Hz, $^2J_{CP}$ = 22 Hz, CPh), 212.0 (CO, $^2J_{CPtrans}$ = 36 Hz, $^2J_{CPcis}$ = 18 Hz), 149.8 (C_{ipso}-Ph), 129.0 (C_o-Ph), 127 (C_m-Ph), 127.2 (C_p-Ph), 19.1 (PMe_3, J_{CP} = 14 Hz); IR 2000 (s), 1926 (s) cm^{-1}. Anal. Calcd for $C_{15}H_{23}ClO_2P_2W$ (M_r 516.56): C, 34.88; H, 4.49. Found: C, 34.96; H, 4.64.

Large-Scale Preparation of 24. A solution of 3 (50.3 g, 0.1 mol) in CH_2Cl_2 (1 L) (2-L round-bottom flask) is cooled to −78 °C, and phosgene is blown over the surface of the stirred solution until the presence of excess phosgene is indicated by IR. The reaction mixture is warmed to 0 °C, and 50% of the solvent is removed in vacuo. Pyridine (40 mL, 0.5 mol) is added, and the flask is vented with a light stream of nitrogen to remove released CO. When the evolution of CO is finished (∼1.5 h), the solvent is removed and the residue washed with hexane and dried. The solid is taken up in CH_2Cl_2 (500 mL) and the solution filtered through a layer of sand. PMe_3 (24 mL, 250 mmol) is added to the filtered solution, and the temperature is raised to 40 °C for 1 h. The solvent is removed in vacuo and the residue washed with hexane (3 × 100 mL) to remove the pyridine. The product is isolated by extraction with ether (800 mL). The filtered ether extract is reduced in volume until the product starts to precipitate. The initial precipitate is redissolved by slight warming. Slow cooling of the ether solution to −78 °C gives large orange crystals of **3** (9.175 g). The extraction/crystallization procedure is repeated six times whereby the mother liquor is recycled (total yield: 42.4 g, 82.1 mmol, 82%).

[W(CPh)Cl(CO)$_2$(dppe)] (25). A solution of **17** (2.61 g, 5.00 mmol) and dppe (2.19 g, 5.5 mmol) in THF (200 mL) is warmed to 40–50 °C until the reaction is completed (IR) (1.5 h). During this time the color turns from orange to bright yellow. The solvent is removed and the solid washed with pentane to remove liberated pyridine. Then the solid is dissolved in CH_3CN and cooled to 0 °C before filtration to remove excess dppe, which is insoluble in CH_3CN. Acetonitrile is removed in vacuo and the product purified by chromatography on silica gel (5 cm × 5 cm, CH_2Cl_2/hexane, 1:1). The product is recrystallized from CH_2Cl_2/hexane to yield a bright yellow microcrystalline powder (3.63 g, 95%) (mp 164–165 °C dec): ^{1}H NMR δ 7.78–6.54 (m, 25 H, C_6H_5), 3.11–2.83 (m, 2 H, CH_2-dppe), 2.78–2.51 (m, 2 H, CH_2-dppe); $^{13}C\{^1H\}$ NMR δ 267.3 ($^2J_{CP}$ = 21.5 Hz, *C*Ph), 212.6 ($^2J_{CPtrans}$ = 44.3 Hz, $^2J_{CPcis}$ = 7.2 Hz, CO), 148.9 (C_{ipso}-*Ph*), 130.0, 128.4 ($C_{o,m}$-*Ph*), 127.2 (C_p-*Ph*), 135.7, 135.0, 132.7, 129.5 (C_6H_5-dppe), 27.5, 27.3, 27.1, 26.9 (CH_2-dppe, J_{CP} = 31.6 Hz, $^2J_{CP}$ = 13.4 Hz); IR 2003 (s), 1934 (s) cm^{-1}. Anal. Calcd for $C_{35}H_{29}ClO_2P_2W$ (M_r 762.86): C, 55.11; H, 3.83. Found: C, 55.36; H, 4.29.

[W(≡CMe)Cl(CO)$_2$(dppe)] (26). A solution of **22** (0.920 g, 2.0 mmol) and dppe (1.31 g, 3.3 mmol) is stirred at room temperature until the reaction is completed (IR) (75 min). During the course of the reaction the color of the solution turned from orange-yellow to yellow. The solvent is removed in vacuo. The product is redissolved in acetonitrile (0 °C) and the resulting solution filtered. Acetonitrile is removed again in vacuo. The product is chromatographed on silica gel (2 cm × 6 cm, −40 °C, CH_2Cl_2/pentane, 1:1, 150 mL). Recrystallization from CH_2Cl_2/ether/pentane gives pale yellow crystals (1.23 g, 88%) (mp 165–168 °C dec): ^{1}H NMR δ 7.69–7.29 (m, 24 H, C_6H_5), 2.8–2.6 (br m, 4 H, PCH_2), 1.35 (t, 3 H, $^3J_{PH}$ = 4.07 Hz, CH_3); $^{13}C\{^1H\}$ NMR δ 279.3 (m, $^1J_{CW}$ = 200 Hz, *C*Ph), 212.9 (d, $^2J_{CP}$ = 43.9 Hz, CO), 135.3, 132.3, 129.9, 128.3 (C_6H_5), 36.0 (CH_3), 26.7 (m, PCH_2); $^{31}P\{^1H\}$ NMR δ 39.45 ($^1J_{PW}$ = 229.52 Hz, $(CH_2PPh_2)_2$); IR 2001 (s), 1928 (s) cm^{-1}. Anal. Calcd for $C_{30}H_{31}ClO_2P_2W$ (M_r 704.82): C, 51.43; H, 4.43. Found: C, 51.16; H, 4.18.

[W(CPh)(O$_2$CCF$_3$)(CO)$_2$(tmeda)] (27). Trifluoroacetic anhydride, $(CF_3CO)_2O$ (0.43 mL, 3.03 mmol), is added dropwise to a cold (−78 °C) solution of **3** (1.51 g, 3.0 mmol) in THF (40 mL). A deep brown-orange color develops immediately. The reaction flask is placed in an ice-water bath. When the color of the solution lightens to a pale yellow, tmeda (4 mL) is added and the solution is allowed to warm to room temperature. Initially, a green color develops which gradually turns deep orange. When the substitution reaction is complete (monitored by IR), the solvent is removed in vacuo and the oily residue washed with pentane (2 × 20 mL). The product is chromatographed on silica gel at −30 °C (3 cm × 8 cm) eluting with CH_2Cl_2. After removal of the solvent the product is recrystallized from CH_2Cl_2/pentane to yield orange crystal (1.30 g, 78%) (mp 146–150 °C dec): ^{1}H NMR δ 7.27 (m, 5 H, Ph), 3.22 (s, br, 6 H, CH_3-tmeda), 2.93 (s, br, 4 H, CH_2-tmeda), 2.76 (s, br, 6 H, CH_3-tmeda); $^{13}C\{^1H\}$ NMR δ 274.1 (J_{CW} = 194.2 Hz, *C*Ph), 221.1 (J_{CW} = 175.9 Hz, CO), 160.4 (O_2-*C*CF$_3$), 149.2, 129.1, 128.1, 127.7 (C_6H_5), 116 (q, J_{CF} = 291.1 Hz, CF_3), 60.7, 57.0 (CH_3-tmeda), 50.5 (CH_2-tmeda); IR 1987 (s), 1895 (s) cm^{-1}. Anal. Calcd for $C_{17}H_{21}F_3N_2O_4W$ (M_r 558.21): C, 36.58; H, 3.79; N, 5.02. Found: C, 36.81; H, 4.02; N, 4.98.

Formation of [W(C(OMe)Ph)(CO)$_5$] (28). NEt_3 (1 mL) and CH_3OH (3 mL) are added successively to the product formed from **3** (0.503 g, 1 mmol) and phosgene (42 mL, gas, 25 °C) at −78 °C. The solvent is removed at room temperature and the residue extracted with hexane. Chromatography on silica gel (2 cm × 5 cm, −20 °C) with hexane as the eluant, and removal of the solvent gives **28** (0.081 g, 18%).

Similarly, **28** is isolated when CH_3OH (2 mL) is added to a solution (−78 °C) of the product from **3** (0.503 g, 1 mmol) and oxalyl chloride (0.11 mL, 1.25 mmol) followed by the previous workup procedure (0.307 g, 69%). **28** is also isolated when a mixture of **3** (1.006 g, 2 mmol), methyl chloroformate (0.31 mL, 4.0 mmol), and triethylamine (0.07 mL, 0.5 mmol) in CH_2Cl_2 is allowed to warm from −78 °C to room temperature followed by the previous workup procedure (0.657 g, 1.48 mmol, 74%).

[W[=C(OC(O)COBr)C$_6$H$_4$OCH$_3$-4](CO)$_5$] for $^{13}C\{^1H\}$ NMR. A solution of $[NEt_4][W(C(O)C_6H_4OCH_3\text{-}4)(CO)_5]$ (0.295 g, 0.50 mmol) in 5 mL CD_2Cl_2 in a 10-mm NMR tube is cooled to −78 °C, and oxalyl bromide (0.048 mL, 0.51 mmol is added dropwise while the NMR tube is shaken. The tube is then placed into the precooled NMR spectrometer: δ 300.5 (J_{CW} = 118.4 Hz, *C*-(OCOCOBr)R), 206.4 (J_{CW} = 107.7 Hz, trans CO), 195.8 (J_{CW} = 129.2 Hz, cis CO), 166.1, 154.0, 149.7, 146.6, 114.7 (C_6H_4 and OCOCOBr), 56.3 (OCH_3).

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