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Reaction of Double Ylide $C(PPh_3)_2$ with $[W(CO)_6]$ – Crystal Structures of $[(CO)_5W(CCPPh_3)]$ and $[(CO)_5W\{\eta^1\text{-}O_2C_2(PPh_3)_2\}]$ and Bonding Analyses of $[TM(CCPR_3)]$ Compounds

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The photochemically generated complex $[(CO)_5W(thf)]$ reacts with $C(PPh_3)_2$ (**1**) to provide the salt $(HC\{PPh_3\}_2)_2[W_2(CO)_{10}]$ (**5**) in high yield by abstraction of a proton from the solvent thf. With $[W(CO)_6]$, a slow reaction in benzene occurs to give a mixture of $[(CO)_5W\{O_2C_2(PPh_3)_2\}]$ (**6**) and the heterocumulene (phosphonioacetylide) complex $[(CO)_5W(CCPPh_3)]$ (**7**) by a Wittig type reaction. Both compounds were characterized by spectroscopic and X-ray diffraction analyses. Theoretical density functional calculations reveal that the ligand $CCPPh_3$ in **7** and in similar complexes is a strong σ-donor but weak π-acceptor.

1. Introduction

Recent theoretical and experimental studies have established the concept of ligand-stabilized carbon atoms (carbones).[1] Among the carbones, carbodiphosphorane $C(PPh_3)_2$ (**1**) was analyzed as containing a divalent carbon(0) atom with two occupied HOMO orbitals, one of σ and one of π symmetry.[2] The syntheses of transition metal carbonyl complexes containing **1** as a ligand were reported very early, but none of the resulting products has been characterized structurally.[3] Later, we found that in the series of group 10 carbonyl compounds, the electron-rich $[Ni(CO)_4]$ reacts with **1** upon formation of the yellow complex $[(CO)_3NiC(PPh_3)_2]$ and the red electron-deficient compound $[(CO)_2NiC(PPh_3)_2]$, which are the only established transition metal carbonyl complexes of **1** so far.[4] The reaction of **1** with platinum compounds $[X_2Pt(cod)]$ (X = Cl, I) resulted in coordination of **1** at the platinum atom and *ortho*-metalation of one or two phenyl groups from PPh_3.[5] Similar Rh^I and Rh^{III} complexes have also been described.[6] Further compounds of the type $M \leftarrow \mathbf{1}$, in which M are main group[7–9] or transition metal Lewis acids,[10–12] can be found in the literature.

Upon reaction of **1** with homoleptic group 7 to 9 carbonyl complexes, nucleophilic attack of **1** at a carbonyl carbon atom occurs in a Wittig type reaction, and no CO substitution product can be found. As a result of this attack, complexes with the neutral heterocumulene or phosphonioacetylide ligand $CCPPh_3$ (**2**) are formed accompanied by the release of Ph_3PO. In summary, two reaction pathways of **1** with transition metal carbonyl complexes were recorded [Equations (1) and (2)].

$$[(CO)_xM\text{–}CO] + \mathbf{1} \rightarrow [(CO)_xMCCPPh_3] + Ph_3PO \qquad (1)$$

$$[(CO)_xM\text{–}CO] + \mathbf{1} \rightarrow [(CO)_xM\text{-}\mathbf{1}] + CO \qquad (2)$$

After reaction of **1** with $[Fe(CO)_5]$, the related complex $[(CO)_4Fe(CCPPh_3)]$ (**3**) was isolated and characterized by X-ray diffraction analysis. The phosphonioacetylide ligand **2** turned out to bind via the terminal carbon atom. In a second isolated trinuclear product, the ligand is bonded in a μ_3,η^2 manner and acts as a six-electron donor.[13] Reaction of **1** with $[Co_2(CO)_8]$ similarly generates **2** incorporated in a tetranuclear cluster having μ_4,η^2-coordination.[14] Correspondingly, with $[Mn_2(CO)_{10}]$, the formation of a Mn-bonded ligand **2** could be confirmed by ^{31}P NMR spectroscopy, but no related product could be isolated.[15] However, the complex $[(CO)_4Mn(CCPPh_3)Br]$ (**4**) was obtained by others and established by crystal structure analysis.[16]

Although compounds containing **2** as the ligand are rare, different approaches outside the Wittig route were reported and studied by X-ray diffraction analysis. Thus, very recently, the cationic ruthenium complex $[RuH(CO)_2(PPh_3)_2(CCPPh_3)]^+$ was obtained by a different reaction route involving $[Me_3SiC_2PPh_3]^+$ as source,[17] and $[(PPh_3)Cl_2Pd(CCPPh_3)]$ was synthesized via dichloroalkyne.[18] Furthermore, a couple of $[TM(CCPR_3)]$ (TM: transition metal) compounds with R other than phenyl were also reported, and their structure was partly established by X-ray diffrac-

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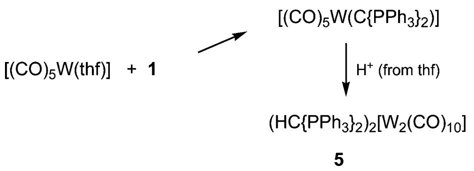
tion analyses;[19] none of the synthetic strategies, however, followed the Wittig route. The synthesis and theoretical analysis of free ligand **2** were reported earlier, and **2** was described as a thermally unstable compound.[20]

Earlier reviews regarding the ligand behavior of **1** were presented by Kaska,[21] Schmidbaur,[22] and in a monograph.[23] The organic chemistry of **1** has been summarized by Bestmann.[24]

In this contribution we report on the outcome of the reaction of **1** with $[W(CO)_6]$ in various solvents and the theoretical analysis of the main product.

2. Results and Discussion

The most successful route to replace a CO group in binary transition metal carbonyl complexes is to photochemically generate the related thf complex and to remove this weakly bound donor molecule by an appropriate ligand L in a subsequent step.[25] When freshly prepared $[(CO)_5W(thf)]$ in thf solution was brought into contact with equimolar amounts of **1** in the same solvent, a clear brown solution was obtained. After several minutes, however, a yellow brown precipitate formed in nearly quantitative yields, which turned out to be the salt $(HC\{PPh_3\}_2)_2[W_2(CO)_{10}]$ (**5**). The formation of **5** is not well understood so far. One possibility includes the formation of the target complex $[(CO)_5W(C\{PPh_3\}_2)]$ in the first step and its subsequent reaction with the solvent as summarized in Scheme 1. Computations (MP2/TZVPP//BP86/SVP as in ref.[1c]) of the high proton affinity of the proposed intermediate complex $[(CO)_5W(C\{PPh_3\}_2)]$, which amounts to 254 kcal mol^{-1} (compared to the proton affinity of **1**: 280 kcal mol^{-1}[1c]), are a further indication for this proposal.



Scheme 1. Formation of complex **5**.

A singlet in the ^{31}P NMR spectrum of **5** at δ = 20.3 ppm stems from the cation $(HC\{PPh_3\}_2)^+$ $(H\leftarrow\mathbf{1})^+$. The IR spectrum shows $\nu(CO)$ bands at low frequencies typical for the carbonylate ion. We further assume that the intermediate complex $[(CO)_5W(C\{PPh_3\}_2)]$ in the first step takes up the abstracted proton to give the cationic complex $[(CO)_5W(HC\{PPh_3\}_2)]^+$, which, however, is not stable and decomposes into $(H\leftarrow\mathbf{1})^+$ and the $[W(CO)_5]$ fragment. The $[W_2(CO)_{10}]^{2-}$ anion may be generated by electron transfer from negatively charged deprotonated thf fragments; however, this process is not yet understood. The nucleophilicity of the cation $(H\leftarrow\mathbf{1})^+$, which still has a lone pair of electrons, is smaller than that for **1**, but we could show in an earlier study that in the absence of coordinating anions $(H\leftarrow\mathbf{1})^+$ can still act as ligand, for example, in the tricationic silver complex $[\{PPh_3\}_2CH\rightarrow Ag\leftarrow CH\{PPh_3\}_2]^{3+}$.[2,26] The action of traces of water in the solvent as proton source can be excluded, because thoroughly dried thf was used and the yield of **5** was quantitative. Furthermore, **1** should have consumed any humidity to give the hydrolysis product $Ph_3PCHP(O)Ph_2$ prior to reaction with $[(CO)_5W(thf)]$; this was not the case, and we learned from various experiments that the cation $(H\leftarrow\mathbf{1})^+$ is similarly produced if an adduct of the type M←**1** (M = main group Lewis acid) is brought into contact with thf. It should be noted that photochemically activated $[Cr(CO)_6]$ and $[M(CO)_6]$ react in the same manner.[27] Earlier reports describe the formation of the adduct $[Ph_3PCHP\{OW(CO)_5\}Ph_2]$,[28] which is not formed in our case. Such a complex would exhibit a pair of doublet signals in the ^{31}P NMR spectrum according to nonequivalent phosphorus atoms, and we believe that this adduct is not the result of the action of water on $[(CO)_5W(C\{PPh_3\}_2)]$ as assumed, but is formed from the reaction of the hydrolysis product $Ph_3PCHP(O)Ph_2$ with $[(CO)_5W(thf)]$. In an earlier report, the formation of $[(CO)_5W(C\{PPh_3\}_2)]$ was described and a signal at δ = 20.7 ppm in the ^{31}P NMR spectrum was assigned to this complex;[3] however, we believe that this signal is due to cation $(H\leftarrow\mathbf{1})^+$, because this value is typical for $(H\leftarrow\mathbf{1})X$ salts.[9]

To avoid potential proton donors such as thf, CH_2Cl_2, dme, or dmso, we studied the reaction of **1** with $[W(CO)_6]$ in benzene. At room temperature, no reaction was observed, as shown by monitoring the progress of the reaction by ^{31}P NMR spectroscopy. Upon activation of the reaction mixture in an ultrasonic bath at 40 °C after about 20 h, the signal of the starting material nearly disappeared in favor of signals (relative intensities in brackets) at –10.7 (0.9), 3.5 (0.07), 16.7 (0.1), 20.6 (0.5), and 25.4 (1.0) ppm. Layering the benzene solution with *n*-pentane gave crystals of $[(CO)_5W\{O_2C_2(PPh_3)_2\}]$ (**6**) and an orange oil. After this oil was kept for several days at room temperature, yellow plates of the phosphonioacetylide complex $[(CO)_5W(CCPPh_3)]$ (**7**) crystallized as the result of a Wittig type reaction [Equation (3)]; crystals are obtained as benzene solvates including one molecule of $OPPh_3$. In the ^{31}P NMR spectrum, the singlets at –10.7 and 25.4 ppm can be attributed to **7** and $OPPh_3$, respectively. Two carbonyl resonances in the ^{13}C NMR spectrum of **7** for *cis* and *trans* CO groups (200.15 and 197.35 ppm) and doublet resonances for the two carbon nuclei of the WCCP spine [δ =190.2 ppm, $^2J(P,C)$ = 16.6 and 83.2 Hz, $^1J(P,C)$ = 179.3 Hz] confirm the crystallographic results; $^{183}W,C$ couplings were only resolved for the CO groups.[29] The formation of **6** with the CO_2 adduct of

$$[W(CO)_6] + \mathbf{1} \rightarrow OPPh_3 + \underset{\mathbf{7}}{[(CO)_5W(CCPPh_3)]} \tag{3}$$

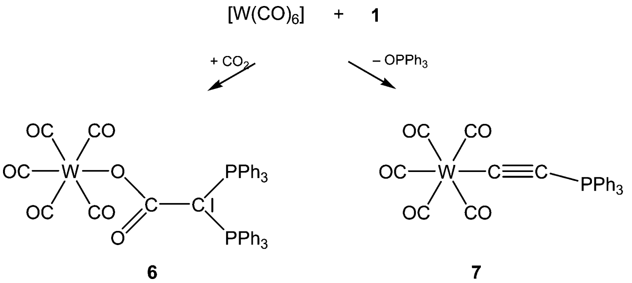
$$[W(CO)_6] + OPPh_3 \rightarrow \text{“}W(CO)_5\text{”} + CO_2 + PPh_3 \tag{4}$$

$$CO_2 + \mathbf{1} \rightarrow O_2C_2(PPh_3)_2 \tag{5}$$

$$\text{“}W(CO)_5\text{”} + O_2C_2(PPh_3)_2 \rightarrow \underset{\mathbf{6}}{[(CO)_5W\{O_2C_2(PPh_3)_2\}]} \tag{6}$$

1 as ligand is unusual under the conditions applied, but it can be rationalized in terms of a subsequent reaction according to Equations (4) to (6).

The phosphane oxide, the second product of the Wittig reaction, can attack a carbonyl group of [W(CO)$_6$] to produce CO$_2$, which is immediately consumed by **1** to give the adduct and potential ligand O$_2$C$_2$(PPh$_3$)$_2$ (O$_2$C←**1**). The formation of O$_2$C←**1** was also observed during the reaction of **1** with [Mn$_2$(CO)$_{10}$] in dme, toluene, or benzene.[15] Compound **6** can also be synthesized directly in high yield from [(CO)$_5$W(thf)] and O$_2$C←**1** as reported recently.[30] We have no hints that under these conditions the carbodiphosphorane complex [(CO)$_5$W(C{PPh$_3$}$_2$)] has formed as an intermediate. Thus, in benzene solution, **1** behaves as a hard base against [W(CO)$_6$] with nucleophilic attack at a carbonyl carbon atom and formation of complex **7** as shown in Scheme 2. First reactions of [Mo(CO)$_6$] with **1** under the same conditions revealed an analogous reaction pathway as shown by ^{31}P NMR spectroscopy; however, no crystalline product could be obtained for final proof. A signal at δ = –12.4 ppm can be attributed to the heterocumulene complex [(CO)$_5$Mo(CCPPh$_3$)]. If thf was used as the solvent in the reaction of [Mo(CO)$_6$] with **1**, surprisingly some carbonato complexes of Mo were isolated in addition to the CO$_2$ adduct [(CO)$_5$Mo{O$_2$C$_2$(PPh$_3$)$_2$}]; these findings will be published elsewhere.



Scheme 2. Formation of tungsten complexes **6** and **7**.

The formation of Wittig product **7** denotes that **1** is a hard base like amines or others, and nucleophilic attack at a carbonyl carbon atom is preferred according to Equation (1). Only with carbonyl compounds [M$_x$(CO)$_y$] of low M–CO dissociation energies {as in [Ni(CO)$_4$]} a CO substitution according to Equation (2) is preferred. Recently, free ligand **2** was prepared and found to be stable only at low temperatures (^{31}P NMR spectrum: δ = –13.7 ppm).[20]

3. Crystal Structures

The structures of compounds **6**·C$_6$H$_6$ and **7**·OPPh$_3$·C$_6$H$_6$ could be confirmed by single-crystal X-ray diffraction analyses. Low yields of orange red crystals of **6**·C$_6$H$_6$ were obtained by layering the benzene solution with *n*-pentane. Upon further addition of *n*-pentane, a pale yellow oil separated, from which yellow plates of **7**·OPPh$_3$·C$_6$H$_6$ crystallized over a period of one week. The related thf solvate of **6** was reported earlier.[30] In Figure 1 the structure of **7** is shown; the solvent and the phosphane oxide have been omitted. Crystallographic data are collected in Table 4; distances and angles are to be found in Table 1.

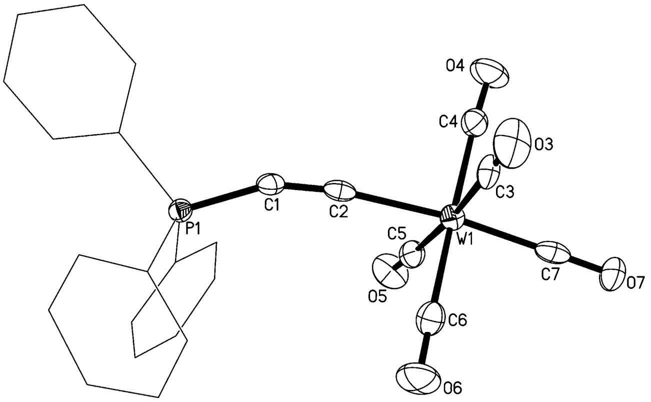


Figure 1. Molecular structure of [(CO)$_5$W(CCPPh$_3$)] (**7**·OPPh$_3$·C$_6$H$_6$) showing the atom numbering scheme; solvent and OPPh$_3$ are omitted. The ellipsoids are drawn at a 40% probability level; the phenyl groups are represented as thin lines, and H atoms are omitted for clarity.

3.1 Crystal Structure of 6·C$_6$H$_6$

The structure of **6**·C$_6$H$_6$ is closely related to that of **6**·2thf, prepared directly from [(CO)$_5$W(thf)] and O$_2$C←**1** in thf solution.[30] The dihedral angle between the P–C–P plane and the O–C–O plane amounts to 9° and is identical with that in the free ligand;[31] a slightly larger angle of 12° was found in **6**·2thf.[30] These differences are clearly influenced by packing effects. The bonding parameters and the representation of the structure have been placed in the Supporting Information.

3.2 Crystal Structure of 7·OPPh$_3$·C$_6$H$_6$

The structure of **7** consists of discrete molecular units without close contacts to the solvent or the OPPh$_3$ molecule. The tungsten atom is in a nearly octahedral environment, and the molecular structure is depicted in Figure 1. The phosphonioacetylide ligand exerts a strong *trans* influence with shortening of the *trans* W–CO bond and elongation of the C–O bond by about 0.07 and 0.045 Å, respectively, with respect to the average of the other four carbonyl ligands. Noticeably, this is not the case for the related [Mn(CO)$_4$Br] or [Fe(CO)$_4$] complexes **4** and **3**, where the differences from the bonding parameters of the other CO ligands are marginal. In contrast, the W–C bond length to the ligand is 0.07 Å longer than the average W–CO length, which is less than those in the related Mn (0.13 Å) and Fe (0.12 Å) complexes. This indicates that the ligand is a strong σ-donor and a weak π-acceptor relative to CO; see also calculations in section 4. A comparison of the most important bond lengths and angles in five transition metal complexes and two main group addition compounds of the terminally bonded heterocumulene is presented in Table 3 (vide infra).

Table 1. Selected bond lengths [Å] and angles [°] in $7{\cdot}OPPh_3{\cdot}C_6H_6$. Calculated values are given in italics for **7** and for **7**H (in brackets).

W1–C7	1.971(6)		W1–C4	2.033(7)	
	2.070	*(2.082)*		*2.074*	*(2.077)*
W1–C3	2.037(6)		W1–C6	2.038(8)	
	2.074	*(2.077)*		*2.074*	*(2.078)*
W1–C5	2.069(6)		W1–C2	2.119(6)	
	2.073	*(2.077)*		*2.139*	*(2.106)*
C1–C2	1.254(7)		C1–P1	1.696(5)	
	1.262	*(1.270)*		*1.684*	*(1.656)*
C3–O3	1.134(6)		C4–O4	1.146(7)	
	1.163	*(1.162)*		*1.163*	*(1.162)*
C5–O5	1.125(6)		C6–O6	1.152(7)	
	1.164	*(1.162)*		*1.163*	*(1.162)*
C7–O7	1.184(6)		P1–C8	1.783(5)	
	1.166	*(1.163)*		*1.836*	
P1–C14	1.801(4)		P1–C20	1.790(5)	
	1.836			*1.836*	
C7–W1–C4	90.2(2)		C7–W1–C3	90.6(2)	
	91.0	*(90.9)*		*91.0*	*(90.9)*
C4–W1–C3	90.5(2)		C7–W1–C6	88.9(2)	
	90.0	*(90.1)*		*91.1*	*(91.0)*
C4–W1–C6	179.1(3)		C3–W1–C6	89.2(2)	
	177.8	*(178.2)*		*89.9*	*(90.0)*
C7–W1–C5	94.1(2)		C4–W1–C5	88.7(2)	
	91.2	*(91.0)*		*90.0*	*(90.0)*
C3–W1–C5	175.3(2)		C6–W1–C5	91.6(2)	
	177.7	*(178.1)*		*90.0*	*(90.0)*
C7–W1–C2	174.1(2)		C4–W1–C2	95.2(2)	
	179.7	*(179.8)*		*88.7*	*(88.9)*
C3–W1–C2	91.7(2)		C6–W1–C2	85.7(2)	
	89.0	*(89.0)*		*89.1*	*(89.2)*
C5–W1–C2	83.8(2)		C2–C1–P1	157.1(4)	
	88.8	*(89.1)*		*179.2*	*(179.3)*
C1–C2–W1	172.0(4)		O3–C3–W1	178.4(5)	
	179.7	*(179.8)*		*179.4*	*(179.3)*
O4–C4–W1	176.6(5)		O5–C5–W1	177.8(5)	
	179.3	*(179.3)*		*179.1*	*(179.2)*
O6–C6–W1	179.4(6)		O7–C7–W1	178.2(5)	
	179.3	*(179.3)*		*179.9*	*(179.9)*
C1–P1–C8	112.2(2)		C1–P1–C20	111.3(2)	
	111.5			*111.5*	
C1–P1–C14	108.1(2)				
	111.5				

Relative to $[(CO)_5W\text{-}L]$ complexes, in which L represents an Arduengo carbene ligand,[32,33] the W–C bond length to the ligand in **7** is about 0.15 Å shorter, indicating a stronger back bonding. However, this may also be due to the bonding of an sp^2 carbon atom in the case of NHC ligands or might have steric reasons. Thus, **7** can be better compared with isocyanide complexes – as stated earlier[14] – which also contain an sp carbon atom linked to the tungsten atom.[34] On the basis of five representative examples of $[(CO)_5WCNR]$ complexes, an average of $W–CNR/W–CO_{tr}$ distances of 2.093/2.016 Å is found, which in **7** amounts to 2.119/1.971 Å. This can be interpreted in terms of a larger σ-donor/π-acceptor ratio of **2** relative to isonitriles.

4. Calculations

We performed some calculations on the free ligand $CCPPh_3$ (**2**) and its metal complexes to shed light on the bonding situation. A comprehensive study of the ligand properties of **2** and its model compound $CCPH_3$ (**2**H) has already been carried out by Bestmann and co-workers,[20] only the key points shall be presented here. Ligand **2** has a rather short C–C bond (**2**H 1.278 Å; **2** 1.275 Å), which is slightly longer than a usual triple bond and a short C–P bond (**2**H 1.665 Å; **2** 1.685 Å) and is similar to that in carbodiphosphorane **1** (1.662 Å)[2] at this level of theory. The P–C–C angle is very close to 180° (**2**H 179.5°; **2** 179.6°), but as described earlier[20] very flexible – indicated by low-lying vibrational bending modes (**2**H 156 cm^{-1}; **2** 80 cm^{-1}). The frontier orbitals of **2**H are shown in Figure 2 (those for **2**Ph are similar). In contrast to Bestmann's work,[20] in both cases we get the HOMO as an orbital with significant lone pair character and HOMO-1/HOMO-2 as degenerated C–P π-bonding orbitals.

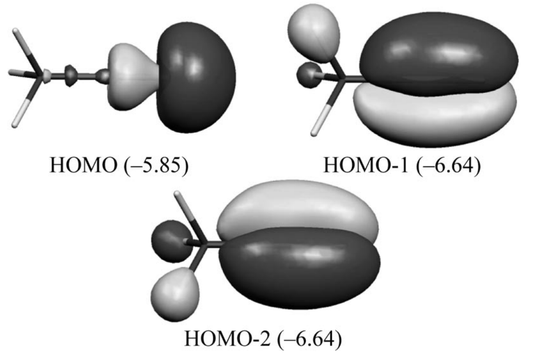

HOMO (–5.85)
HOMO-1 (–6.64)
HOMO-2 (–6.64)

Figure 2. Highest lying occupied molecular orbitals of $CCPH_3$ (**2**H). Orbital energies are given in eV.

In agreement with earlier results,[20] charge distribution as indicated by natural bond orbital (NBO) analysis shows a high negative charge on C1 (**2**H/**2**: –0.96 e) and a nearly neutral C2 (**2**H/**2**: +0.10 e). As the coordination chemistry of this complex shows, the frontier orbitals are thus a much better indicator for the ligand properties than the partial charges, which would indicate C1 as ligating center.

We calculated complex **7** and the model complex **7**H (with **2**H instead of **2** as ligand) together with two other models of structurally characterized complexes, namely $[Fe(CO)_4(2H)]$ (**3**H) and $[(CO)_4Mn(2H)Br]$ (**4**H), to characterize the ligand properties. The comparison to the experimental bonding parameters in Table 1 shows good agreement – the flexible CCP angle was discussed in the first paragraph of section 4. The second set of theoretical values in Table 1 belongs to model compound **7**H, exemplifying the validity of reducing the ligand size for the following bonding analysis by good agreement with the real complex. Figure 3 shows the frontier orbitals of **7**H, which give a first indication of the ligand properties.

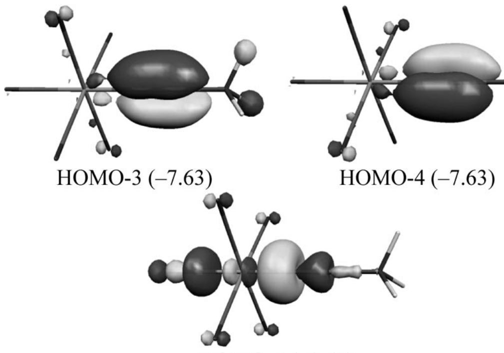
There is a strong σ-donation from the HOMO of the ligand towards the metal center in HOMO-5 and nearly unchanged π-orbitals in HOMO-3 and HOMO-4; HOMO, HOMO-1, and HOMO-2 show mainly tungsten d orbital character. A quantification of these trends can be achieved by applying energy decomposition analysis (EDA), success-

Table 2. Energy decomposition analysis (EDA) of the metal–ligand bond of model compounds by applying C_s symmetry. Energy values are given in kcal mol^{-1} at the BP86/TZ2P level of theory.

$TM–C–C–PH_3 \rightarrow TM + C–C–PH_3$

	3H		**4H**		**7H**		**7H**[a]	
ΔE_{int}	–74.0		–59.7		–66.2		–50.9	
ΔE_{Pauli}	168.2		172.8		150.2		124.1	
ΔE_{elstat}[b]	–143.0	(59.0%)	–140.9	(60.6%)	–137.4	(63.5%)	–92.7	(53.0%)
ΔE_{orb}[b]	–99.2	(41.0%)	–91.6	(39.4%)	–79.1	(36.5%)	–82.3	(47.0%)
ΔE_{σ}[c]	–80.7	(81.3%)	–77.4	(84.5%)	–62.0	(78.4%)	–58.8	(71.5%)
ΔE_{π}[c]	–18.5	(18.7%)	–14.2	(15.5%)	–17.1	(21.6%)	–23.4	(28.5%)
ΔE_{π} (TM → L)[d]	–17.6	(88.4%)	–13.1	(83.9%)	–15.6	(87.0%)	–22.4	(92.4%)
ΔE_{π} (L → TM)[d]	–2.3	(11.6%)	–2.5	(16.1%)	–2.3	(13.0%)	–1.9	(7.6%)
ΔE_{prep}	7.9		10.2		3.2		4.2	
TM ΔE_{prep}	7.8		9.6		3.2		3.6	
$CCPH_3$ ΔE_{prep}	0.1		0.5		0.1		0.6	
ΔE (= $-D_e$)	–66.0		–49.5		–63.0		–46.7	
d(M–L)	1.834		1.886		2.083		2.057	

[a] Analysis of the M–CO bond by choosing the fragments as $(CO)_4WCCPPH_3$ and CO. [b] The percentage values in parentheses give the contribution to the total attractive interactions (ΔE_{elstat} + ΔE_{orb}). [c] The percentage values in parentheses give the contribution to the orbital interaction (ΔE_{orb}). [d] The percentage values in parentheses give the contribution to the total nonsynergetic π-type interactions ΔE_{π} (TM → L) + ΔE_{π} (L → TM).


HOMO-3 (–7.63) HOMO-4 (–7.63)

HOMO-5 (–8.67)

Figure 3. Highest lying occupied molecular orbitals of **7**H. Orbital energies are given in eV.

fully used in the past for metal–ligand bonding analysis.[35] Results for model systems **3**H, **4**H, and **7**H are shown in Table 2.

The results show that the bonding is rather similar in all three complexes and that orbital interaction accounts for roughly 40% of the interaction energy. Breaking down this value shows that – as indicated by the frontier orbitals – the main contribution comes from σ-bonding. The π-bonding accounts for 15–21% of the orbital interaction and stems from metal-to-ligand back-donation as found by conducting an orbital deletion procedure we applied earlier to various transition metal carbene complexes.[36] The trend for the dissociation energies is **3**H > **7**H > **4**H. This is not altered by looking at the interaction energy alone, which lacks fragment relaxation. A comparison with dissociation of the *trans*-CO ligand in **7**H (Table 2, right column) shows that **2**H is a stronger σ-donor but a weaker π-acceptor than CO and forms significantly stronger bonds. This interpretation is in line with a very recent frontier orbital study by Hill et al.[17] with the only difference that we could not establish strong π-donor abilities in our quantitative bonding analysis.

5. Conclusion and Outlook

As yet, all our attempts have failed to isolate the homoleptic group 6 complexes $[(CO)_5M(C\{PPh_3\}_2)]$, although theoretical calculations predict the compounds to be stable. Compound **1** is a strong base, and its proton affinity was calculated to be 280 kcal mol^{-1}. However, for the postulated complex $[(CO)_5W(C\{PPh_3\}_2)]$ a similarly high proton affinity of 254 kcal mol^{-1} was estimated, which results from the existence of the second HOMO orbital left at the central carbon atom of ligated **1**, which changes the properties of the addition compound dramatically. For low-valent transition metals in a M←**1** complex, repulsion between M and **1** is expected, whereas for metals in high oxidation states the possibility of a four-electron-donating ligand is given.[10,37]

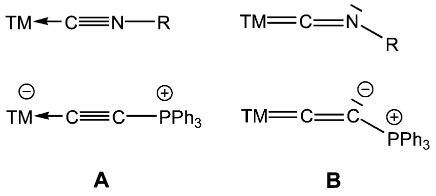
With the preparation of **7** the number of transition metal compounds with the terminally bonded phosphonioacetylide ligand **2** has increased to seven examples, if we include the compounds $OC_2(PPh_3)$ and $SC_2(PPh_3)$. Further compounds with the $CC(PR_3)$ core but with other PR_3 groups are $Ph_3BC_2(PPh_2Me)$[38] and related transition metal complexes with R other than phenyl.[19] Parameters similar to those depicted in Table 3 were found. As yet, the access to complexes with the $CC(PR_3)$ ligand follows either the Wittig route by the action of **1** and C–C bond formation, as

Table 3. Comparison of bond lengths [Å] and angles [°] in $[TM(CCPPh_3)]$ compounds.

TM	$(CO)_5W$ (**7**)	$Br(CO)_4Mn$ (**4**)	$(CO)_4Fe$ (**3**)	$RuH(CO)_2(PPh_3)_2^+$	$(PPh_3)Cl_2Pd$	S	O
P–C	1.696(5)	1.679(13)	1.694(3)	1.698(6)	1.71(1)	1.677	1.648
C–C	1.254(7)	1.216(14)	1.211(3)	1.235(9)	1.23(2)	1.209	1.201
C–C–P	1.571(4)	1.640(12)	1.621(3)	1.724(5)	1.755(8)	1.680	1.455
E–C–C	1.720(4)	1.763(12)	1.790(2)	1.774(5)	1.755(9)	1.783	1.756
Reference	this work	[16]	[13]	[17]	[18]	[39]	[40]

reported here, or a C_2 transfer to a metal via functional acetylenes. However, no complex has been built up so far starting from free ligand **2**.

The C–C bond lengths in the majority of the complexes in Table 3 do not change markedly, being close to a triple bond. The C–C–P bond angles exhibit great flexibility but are also close together, and deviations from the theoretically predicted linearity (see preceding section) may be caused by packing effects. However, the C–C bond length of **7** is slightly larger and the C–C–P bond angle in **7** is more acute. As shown in Scheme 3, for complexes with **2** or isonitriles as ligands, two canonical structures involving a linear (**A**) or a bent (**B**) geometry can be formulated. The deviations from linearity in the experimental structures point to the inclusion of some **B** character in the bond description (by decrease in the C–C triple bond character), which is in line with the metal-to-ligand back-donation found in the calculations. However, the effects are not strong enough to result in a bent gas-phase geometry in the calculations.



Scheme 3. Bonding situation in isocyanide and phosphonioacetylide compounds.

As mentioned above, two complexes are described in which **2** is also bonded in a bridging manner. This bonding mode also applies to isonitriles, and even to CO,[14,38] and emphasizes the isolobal and isoelectronic nature of these ligands.

Quantitative theoretical bonding analysis of the heterocumulene ligand $CCPR_3$ agrees with previous qualitative arguments that this is a strong σ-donor ligand and a weak π-acceptor not only in the new complex **7**, but also in previously synthesized complexes. In contrast to results of very recent studies, we could not find significant π-donor properties.

6. Experimental Section

General: All operations were carried out under an argon atmosphere in dried and degassed solvents by using Schlenk techniques. The solvents were thoroughly dried and freshly distilled prior to use. The IR spectra were run with a Nicolet 510 spectrometer. Analyses were performed by the analytical service of our department. For the ^{31}P NMR spectra we used the instrument Bruker AC 300. Compound **1** was prepared according to a modified literature procedure.[41] Commercially available $[W(CO)_6]$ was sublimed prior to use. Crystallographic details are summarized in Table 4. CCDC-750420 ($\mathbf{6}\cdot C_6H_6$) and -750421 ($\mathbf{7}\cdot OPPh_3\cdot C_6H_6$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Reaction of 1 with $[W(CO)_5(thf)]$: A solution of $[W(CO)_6]$ (0.74 g, 2.1 mmol) in about thf (100 mL) was irradiated for 7 h with a high-pressure mercury lamp. The yellow solution of the resulting $[W(CO)_5(thf)]$ complex was poured into a thf solution of **1** (1.1 g, 2.1 mmol). The color of the solution turned to orange, and after about 30 min of stirring at room temperature, an orange precipitate formed, which was filtered and dried in vacuo. The supernatant thf solution showed peaks in the ^{31}P NMR spectrum at $\delta = 20.3$ (main signal), 16.1, and –4.9 (unreacted **1**) ppm. According to the spectroscopic data, the precipitate turned out to be salt **5** (90% yield), which is only slightly soluble in thf. ^{31}P NMR (300 MHz, DCM, 25 °C): $\delta = 20.3$ ppm, which is due to the cation $[HC\{PPh_3\}_2]^+$. IR (Nujol mull): $\tilde{\nu} = 1894$ (vs), 1858 (vs), 1836 (vs), 1813 (vs), 1773 (s), 1481 (s), 1439 (s), 1377 (m), 1296 (m), 1279 (s), 1233 (m), 1184 (w), 1099 (s), 1061 (w), 1030 (w), 1013 (m), 991 (s), 747 (m), 715 (s), 691 (s), 559 (m), 529 (m), 515 (m), 496 (m) cm^{-1}. The bands at 1030, 1013, and 991 cm^{-1} are typical for the cation $[HC\{PPh_3\}_2]^+$. $C_{48}H_{32}O_{10}P_4W_2$ (1259.41): calcd. C 45.77, H 2.48; found C 44.13, H 2.64.

Reaction of 1 with $[W(CO)_6]$ in Benzene: A mixture of $[W(CO)_6]$ (0.31 g, 0.9 mmol) with **1** (0.47 g, 0.9 mmol) in benzene (about 4 mL) was irradiated in an ultrasonic bath at ca. 40 °C for 24 h. A clear orange solution was obtained with small amounts of an insoluble material. The ^{31}P NMR spectrum of this solution showed signals at 25.8, 20.6, 16.7, 3.5 (PPh_3), –10.7 ppm in a 1:0.5:0.1:0.07:0.9 ratio. The solution was filtered and layered with *n*-pentane. Pale yellow crystals of $\mathbf{6}\cdot C_6H_6$ separated along with an orange oil. $\mathbf{6}\cdot C_6H_6$ (yield, not optimized, 0.04 g): ^{31}P NMR (300 MHz, C_6H_6, 25 °C): $\delta = 20.7$ (s) ppm. IR (Nujol mull): $\tilde{\nu} = 2070$ (w), 1941 [vs, br (unresolved ν, CO)] , 1589 (m), 1481 (s), 1437 (vs), 1335 (w), 1312 (m), 1277 (w), 1202 (s), 1181 (s), 1157 (m), 1109 (s), 1071 (m), 1028 (m), 997 (m), 856 (m), 841 (m), 756 (s), 745 (s), 721 (vs), 677 (vs), 594 (s), 581 (s), 542 (s), 525 (s), 492 (s), 451 (m), 442 (m) cm^{-1}. The oil was separated and extracted with benzene, and the solution was layered with *n*-pentane. After several days, yellow plates of $\mathbf{7}\cdot OPPh_3\cdot C_6H_6$ separated (yield, not optimized, 0.12 g). The supernatant solution still showed peaks of **7** and $OPPh_3$. The product was filtered and dried in vacuo: ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 200.2$ (s, $^2J_{W,C} = 128.1$ Hz, CO_{trans}), 197.4 (s, $^2J_{W,C} = 125.1$ Hz, CO_{cis}), 190.2 (d, $^2J_{P,C} = 16.6$ Hz, $W\mathbf{C}CPPh_3$), 139.0 to 123.9 (m, Ph), 83.2 (d, $^1J_{P,C} = 179.3$ Hz, $WC\mathbf{C}PPh_3$) ppm. ^{31}P NMR (300 Mz, C_6H_6, 25 °C): $\delta = 24.8$ (s, $O\mathbf{P}Ph_3$), –11.7 (s, $C\mathbf{P}Ph_3$) ppm. IR (Nujol mull): $\tilde{\nu} = 1985$ (s), 1975 (s), 1906 {vs, br [unresolved ν(CO)]}, 1589 (w), 1576 (w), 1483 (m), 1439 (s), 1121 (s), 1111 (s), 845 (m), 754 (m), 745 (m 721 s), 696 (s), 689 (m), 596 (s), 579 (s), 538 (s), 522 (m), 495 (m) cm^{-1}. $C_{43}H_{30}O_6P_2W$ (888.45) ($\mathbf{7}\cdot OPPh_3$): calcd. C 58.13, H 3.40; found C 57.67, H 3.47.

Table 4. Crystal data and structural refinement details.

	6·C_6H_6	**7**·$OPPh_3$·C_6H_6
Formula	$C_{49}H_{36}O_7P_2W$	$C_{49}H_{36}O_6P_2W$
Diffractometer	IPDS I (Stoe)	IPDS I (Stoe)
Radiation	Mo-K_α	Mo-K_α
MW [g mol^{-1}]	982.57	966.57
a [Å]	28.866(2)	10.988(1)
b [Å]	13.171(1)	11.151(1)
c [Å]	11.042(1)	20.008(2)
α [°]	90	88.67(1)
β [°]	90	77.88(1)
γ [°]	90	61.74(1)
Crystal size [mm]	0.42 × 0.21 × 0.12	0.25 × 0.2 × 0.11
Volume [Å^3]	4198(1)	2102.9(3)
Z	4	2
$d_{calcd.}$ [g cm^{-3}]	1.555	1.526
Crystal system	orthorhombic	triclinic
Space group	$Pna2_1$ (Nr. 33)	$P\bar{1}$ (Nr. 2)
Temperature [K]	193	193
μ [cm^{-1}]	28.81	28.72
$2\theta_{max}$ [°]	51.86	51.84
Index range	$-35 \leq h \leq 35$	$-13 \leq \mathrm{h} \leq 13$
	$-16 \leq k \leq 16$	$-13 \leq k \leq 13$
	$-13 \leq l \leq 13$	$-24 \leq \mathrm{l} \leq 24$
Number of reflections collected	38065	20824
Number of independent reflections (R_{int})	8113 (0.0458)	7633 (0.056)
Number of observed reflections with $F_o > 4\sigma(F_o)$	5852	4965
Parameters	533	524
Absorption correction	numerical	numerical
Structure solution	direct methods, *SHELXS-97*[42]	direct methods, *SIR-92*[43]
Refinement against F^2	*SHELXL-97*[44]	*SHELXL-97*[44]
H atoms	calculated positions with a common displacement parameter	
Flack parameter	–0.031(5)	–
R_1	0.0268	0.0327
wR_2 (all data)	0.0458	0.0539
Max. electron density left [e Å^{-3}]	2.299	0.997

7. Computational Details

Geometry optimizations without symmetry constraints have been carried out by using the Gaussian03 optimizer[45] together with TurboMole5[46] energies and gradients at the BP86[47]/def-SVP[48] level of theory. For the phenyl rings of PPh_3 groups, a minimal basis set has been used (benzene BS) except for the α-C atom. Stationary points were characterized as minima by calculating the Hessian matrix analytically at this level of theory.[49] Kohn–Sham orbitals have been taken from these calculations. The resolution of identity method has been applied.[50] The NBO[51] analyses have been carried out with the internal module of Gaussian03 at the BP86/TZVPP level of theory.

For the bonding analysis, some molecules have been optimized with the C_s symmetry constraint with the program package ADF2006.01[52] As above, BP86 was chosen by applying uncontracted Slater-type orbitals (STOs) as basis functions.[53] The latter basis sets for all elements have triple-ζ quality augmented by two sets of polarization functions (ADF basis set TZ2P). Core electrons (i.e., 1s for second- and [He]2s2p for third-period atoms) were treated by the frozen-core approximation. This level of theory is denoted by BP86/TZ2P. An auxiliary set of s, p, d, f, and g STOs was used to fit the molecular densities and to represent the Coulomb and exchange potentials accurately in each self-consistent field (SCF) cycle.[54] Scalar relativistic effects have been incorporated by applying the zeroth-order regular approximation (ZORA) in all ADF calculations.[55]

The interatomic interactions were investigated by means of an energy decomposition analysis (EDA) developed independently by Morokuma[56] and by Ziegler and Rauk.[57] The bonding analysis focuses on the instantaneous interaction energy, ΔE_{int}, of a bond A–B between two fragments A and B in the particular electronic reference state and in the frozen geometry of AB. This interaction energy is divided into three main components [Equation (7)].

$$\Delta E_{int} = \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{orb} \qquad (7)$$

The term ΔE_{elstat} corresponds to the quasiclassical electrostatic interaction between the unperturbed charge distributions of the prepared atoms and is usually attractive. The Pauli repulsion, ΔE_{Pauli}, is the energy change associated with the transformation from the superposition of the unperturbed electron densities of the isolated fragments to the wave function, which properly obeys the Pauli principle through explicit antisymmetrization and renormalization (N = constant) of the product wavefunction.[52a] ΔE_{Pauli} comprises the destabilizing interactions between electrons of the same spin on either fragment. The orbital interaction, ΔE_{orb}, accounts for charge transfer and polarization effects.[58] The ΔE_{orb} term can be decomposed into contributions from each irreducible representation of the point group of the interacting system. The molecules investigated show C_s symmetry, which makes it possible to distinguish between σ-contributions (a′) and π-contributions (a′′).

$$\Delta E_{orb}\ (C_s) = \Delta E_\sigma(a') + \Delta E_\pi(a'') \qquad (8)$$

To obtain the bond dissociation energy (BDE) D_e (by definition having the opposite sign of ΔE), the preparation energy, ΔE_{prep}, which gives the relaxation of the fragments into their electronic and geometrical ground states, must be added to ΔE_{int} [Equation (9)].

$$\Delta E\ (= -D_e) = \Delta E_{int} + \Delta E_{prep} \qquad (9)$$

Further details on the EDA method and its application to the analysis of the chemical bond[59] can be found in the literature.

Supporting Information (see footnote on the first page of this article): Crystal structure, structural details of **6**·C_6H_6 and cartesian coordinates of computationally investigated compounds.

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