

Molybdenum and tungsten complexes of the neutral tripod ligands HC(pz)₃ and MeC(CH₂PPh₂)₃

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Abstract

Starting from [M(CO)₆], seven-coordinated complexes of tungsten and molybdenum containing the facially coordinating ligands HC(pz)₃ (**1**) and MeC(CH₂PPh₂)₃ (**2**) were obtained in a two-step reaction sequence. The complexes have a 4:3 piano stool geometry with almost perfect C_{3v} symmetry in the crystal. In solution, they show the typical fluxional behavior for seven-coordinated complexes even at low temperature. Complete oxidative decarbonylation occurs when [HC(pz)₃Mo(CO)₃] (**4**) or [MeC(CH₂PPh₂)₃Mo(CO)₃] (**6**) are treated with an excess of I₂ or Br₂.

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1. Introduction

Besides Cp, tris(pyrazolyle)borate (Tp) is the most widely used monoanionic facially coordinating tripod ligand in organometallic chemistry. Due to its shape, the Tp ligand and analogous systems are often called scorpionates. Since its first synthesis by Trofimenko in the late 1960s, a variety of different organometallic complexes containing Tp have been prepared [1–6]. Recently, homoscorpionate ligands with thioether [7,8], thiocarbonyl [9,10] or phosphine [11,12] donors have been reported, as well as NNS and NNO heteroscorpionates [13–15]. While the former were developed to obtain Tp analogues with a softer donor atom, the latter ones were introduced to act as molecular models for metalloproteins.

However, only few reports deal with the neutral analogue of Tp, tris(pyrazolyle)methane HC(pz)₃ (**1**), although its ability to act as a tridentate ligand in transition metal complexes has been observed virtually at the same time [16]. This is partially due to the difficulties associated with the syntheses of **1**, limiting the application compared to Tp

so far. Since a new, easy multi-gram scale preparation method has been reported, the interest on this neutral tripod ligand will increase [17,18].

Mo and W carbonyl complexes containing the Tp ligand have been extensively studied, and some similar HC(pz)₃ (**1**) complexes were prepared to compare the reactivities towards oxidative addition. This would open a new route to Mo(II) and W(II) as well as Mo(III) complexes. Furthermore, the tripod phosphine ligand 1,1,1-tris(diphenylphosphinomethyl)ethane MeC(CH₂PPh₂)₃ (**2**) was also employed in this study to compare the different donor atoms nitrogen and phosphorus.

2. Results

2.1. Precursors

The ligands **1** and **2** were prepared according to the published procedures [18,19]. The reaction of the hexacarbonyls [Mo(CO)₆] and [W(CO)₆] with **1** in refluxing DMF proceeds smoothly to give the neutral tricarbonyl complexes [HC(pz)₃M(CO)₃] (**3** and **4**) in high yields as yellow, air-stable solids [16]. The same reaction conditions can be

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used for the preparation of $[\text{MeC}(\text{CH}_2\text{PPh}_2)_3\text{M}(\text{CO})_3]$ (**5** and **6**), which are isolated as white, air-stable powders. This one step method is superior to previously reported synthetic procedures [20,21], giving higher yields in a shorter time period (Equation 1).

2.2. Crystal and molecular structure of **5**

Colorless, block-shaped crystals suitable for X-ray analysis of $[\text{MeC}(\text{CH}_2\text{PPh}_2)_3\text{W}(\text{CO})_3]$ (**5**) were grown from dichloromethane/pentane at 20 °C. The complex crystallizes in the hexagonal space group R3 and has a crystallographic C_3 symmetry. Due to steric interaction, the octahedral geometry around the tungsten atom is distorted, with C1–W–C1A and P1–W–P1A angles significantly smaller than 90°. All these features, including the C_3 symmetry, have already been observed in the crystal structure of **6** [19] (see Fig. 1).

2.3. Oxidative addition

Reaction of $[\text{HC}(\text{pz})_3\text{M}(\text{CO})_3]$ (**3** and **4**) with I_2 or Br_2 gives the seven coordinated cationic complexes $[\text{HC}(\text{pz})_3\text{M}(\text{CO})_3\text{X}]\text{X}$ (M = W **7a, b**; Mo **8a, b**) as yellow or brown powders in good to excellent yields after 2 h at 20 °C (Equation 2, left). The iodo complexes **7a** and **8a** are stable as solids, while the bromo complexes are more sensitive towards air, decomposing within 3–5 days upon exposure.

When $[\text{MeC}(\text{CH}_2\text{PPh}_2)_3\text{M}(\text{CO})_3]$ (**5** and **6**) is reacted with 1 equiv. of I_2 or Br_2 , IR spectroscopy reveals the formation of a 1:1 mixture of the starting material and the seven coordinated product. A second equivalent of halogen is necessary to complete the reaction within 2 h at 20 °C (Equation 2, right). The product complexes $[\text{MeC}(\text{CH}_2\text{PPh}_2)_3\text{M}(\text{CO})_3\text{X}]_3$ (M = W **9a, b**; Mo **10a**) are isolated in high yields as orange red or brown powders.

The $\text{HC}(\text{pz})_3$ complexes are more stable in solution than the $\text{MeC}(\text{CH}_2\text{PPh}_2)_3$ complexes, allowing a complete characterization by IR and NMR spectroscopy even in acetone. The phosphine complexes **9a**, **9b** and **10a** can be isolated, but their characterization is difficult due to dehalogenation and subsequent decomposition. Only **9a** is stable enough to perform ^{13}C NMR spectroscopy, and even there, reformed starting material **5** is always observed within 6–8 h.

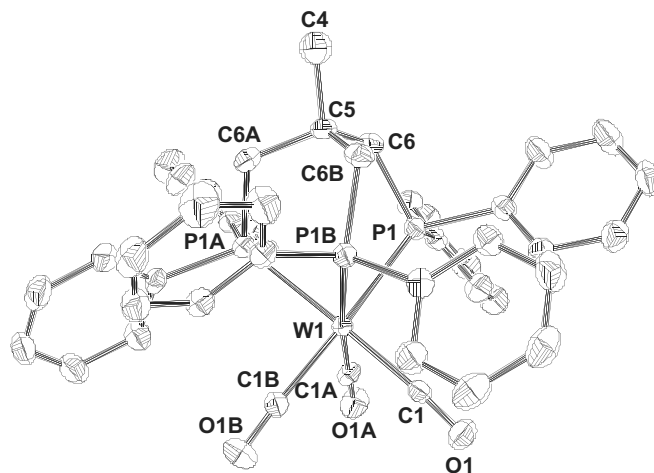


Fig. 1. Molecular structure of $[\text{MeC}(\text{CH}_2\text{PPh}_2)_3\text{W}(\text{CO})_3]$ (**5**), selected bond lengths (pm) and angles (°): W1–C1 197.8(4), W1–P1 250.69(11), C1–O1 114.1(4), P1–C6 185.2(3); C1–W1–P1 98.70(11), C1A–W1–P1 91.99(12), C1B–W1–P1 174.97(13), C1–W1–C1A 85.41(16), W1–C1–O1 175.4(4), P1–W1–P1A 84.12(4), W1–P1–C6 111.20(11).

2.4. Crystal and molecular structure of **7a**

See Fig. 2.

2.5. Crystal and molecular structure of **7b**

See Fig. 3.

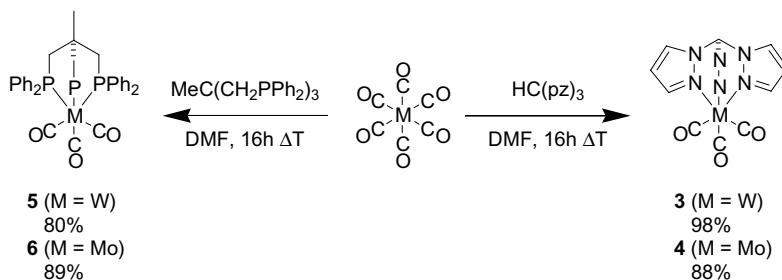
2.6. Crystal and molecular structure of **8a**

See Fig. 4.

2.7. Crystal and molecular structure of **9a**

See Fig. 5.

Crystals suitable for X-ray analysis have either been obtained from acetone/diethyl ether at 20 °C (**7a**) or –30 °C (**7b, 8a, 9a**). In **7b** and **9a**, acetone is found in the unit cell. The composition of the counter ions (X^- or X_3^-) is proven by the crystal structure. The two iodo complexes $[\text{HC}(\text{pz})_3\text{M}(\text{CO})_3\text{I}]\text{I}$ (M = W **7a**, Mo **8a**) are isostructural (monoclinic space group $P2(1)/c$, nearly identical cell parameters), while the bromo complex



Equation 1. Synthesis of the tricarbonyl complexes **3–6**.

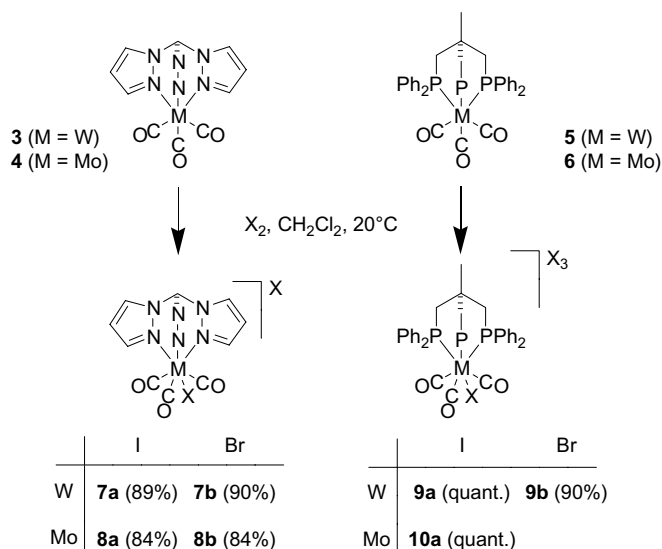
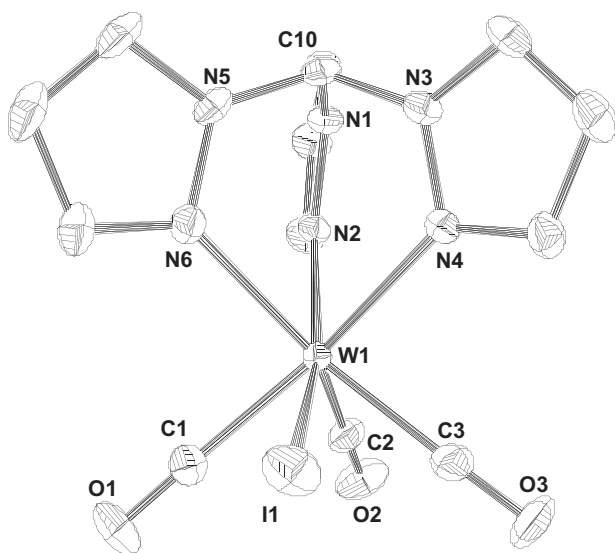
Equation 2. Oxidative addition of I₂ and Br₂.

Fig. 2. Structure of the cation of $[\text{HC}(\text{pz})_3\text{W}(\text{CO})_3\text{I}]\text{I}$ (**7a**), selected bond lengths (pm) and angles ($^\circ$): W1–C1 199.4(4), W1–C2 198.3(4), W1–C3 198.6(4), W1–I1 282.50(3), W1–N2 221.8(3), W1–N4 222.6(3), W1–N6 222.4(3), C1–O1 114.1(5), C2–O2 114.4(5), C3–O3 114.2(5), N1–N2 136.8(4), N3–N4 135.5(4), N5–N6 136.5(4); W1–C1–O1 178.3(4), W1–C2–O2 178.2(4), W1–C3–O3 178.0(4), W1–N2–N1 121.1(2), W1–N4–N3 121.7(2), W1–N6–N5 121.0(2), I1–W1–C1 77.07(11), I1–W1–C2 125.52(11), I1–W1–C3 74.97(12), I1–W1–N2 158.09(8), I1–W1–N4 87.32(8), I1–W1–N6 84.40(8), C1–W1–N2 110.76(13), C1–W1–N4 161.55(14), C1–W1–N6 88.12(14), C2–W1–N2 76.24(13), C2–W1–N4 124.10(14), C2–W1–N6 138.21(13), C3–W1–N2 120.80(14), C3–W1–N4 82.20(13), C3–W1–N6 153.60(14).

$[\text{HC}(\text{pz})_3\text{W}(\text{CO})_3\text{Br}]\text{Br}$ (**7b**) crystallizes together with one molecule of acetone in the monoclinic space group $C2/c$.

The metal centers show a four-legged 4:3 piano stool arrangement of the ligands. As observed for $[\text{TpMo}(\text{CO})_3\text{Br}]$ [22], the halogen occupies a position *trans* to one of the donor atoms of the tripod ligand, N or P. There-

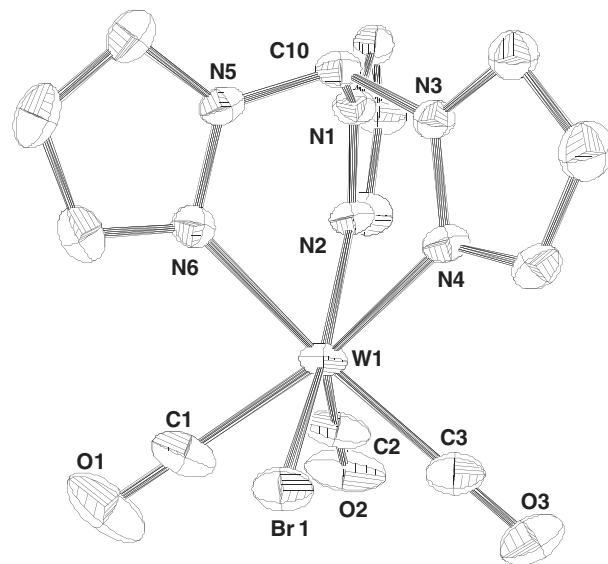


Fig. 3. Structure of the cation of $[\text{HC}(\text{pz})_3\text{W}(\text{CO})_3\text{Br}]\text{Br}$ (**7b**), selected bond lengths (pm) and angles ($^\circ$): W1–C1 199.6(11), W1–C2 198.5(10), W1–C3 199.6(11), W1–Br1 262.59(10), W1–N2 221.7(7), W1–N4 221.7(8), W1–N6 221.4(8), C1–O1 113.4(14), C2–O2 113.2(13), C3–O3 113.9(13), N1–N2 137.1(10), N3–N4 135.7(10), N5–N6 137.1(10); W1–C1–O1 178.7(10), W1–C2–O2 176.0(10), W1–C3–O3 178.8(10), W1–N2–N1 120.9(6), W1–N4–N3 121.9(5), W1–N6–N5 121.4(6), Br1–W1–C1 75.0(3), Br1–W1–C2 123.5(3), Br1–W1–C3 77.1(3), Br1–W1–N2 159.99(19), Br1–W1–N4 85.2(2), Br1–W1–N6 86.1(2), C1–W1–N2 116.2(4), C1–W1–N4 155.1(4), C1–W1–N6 84.0(4), C2–W1–N2 76.5(3), C2–W1–N4 134.1(4), C2–W1–N6 131.5(4), C3–W1–N2 113.1(4), C3–W1–N4 84.2(3), C3–W1–N6 157.6(3).

fore, the $\text{HC}(\text{pz})_3$ complexes closely approximate C_S symmetry with I or Br, C2–O2, N1–N2 pz ring, W or Mo, and C10 defining the mirror plane. The bond distances and angles for the $\text{HC}(\text{pz})_3$ complexes **7a**, **7b** and **8a** are almost identical within the margin of error, which is in contrast to $[\text{TpMo}(\text{CO})_3\text{Br}]$, where the Mo–C (195.7(7) pm) and C–O (115.5(8) pm) bond distances *trans* to Br differ significantly compared to the Mo–C (198.7(7) and 199.9(8) pm) and C–O (114.3(9) and 113.1(8) pm) distances in *cis*-position. However, the same trend as for $[\text{TpMo}(\text{CO})_3\text{Br}]$ is observed in **9a** with the *trans* W–C bond by some 4 pm shorter and the *trans* C–O by 1 pm longer than their *cis* counterparts.

Protonation of the tricarbonyl complexes **3–6** with HBF_4 occurs exclusively at the metal (Equation 3). Other acids, like MeSO_3H or CF_3COOH , were not strong enough to protonate the metal.

$[\text{HC}(\text{pz})_3\text{M}(\text{CO})_3\text{H}]\text{BF}_4$ (M = W **11**, Mo = **12**) are isolated as blue (**11**) or yellow (**12**), air-sensitive powders in quantitative yields, while $[\text{MeC}(\text{CH}_2\text{PPh}_2)_3\text{M}(\text{CO})_3\text{H}]\text{BF}_4$ (M = W **13**, Mo = **14**) are cream-colored solids. The hydrido complexes are stable in the non-coordinating, polar solvent dichloromethane. If THF, diethyl ether or acetone is used during workup or as solvent for spectroscopic characterization, the complexes are slowly deprotonated, giving rise to the starting materials.

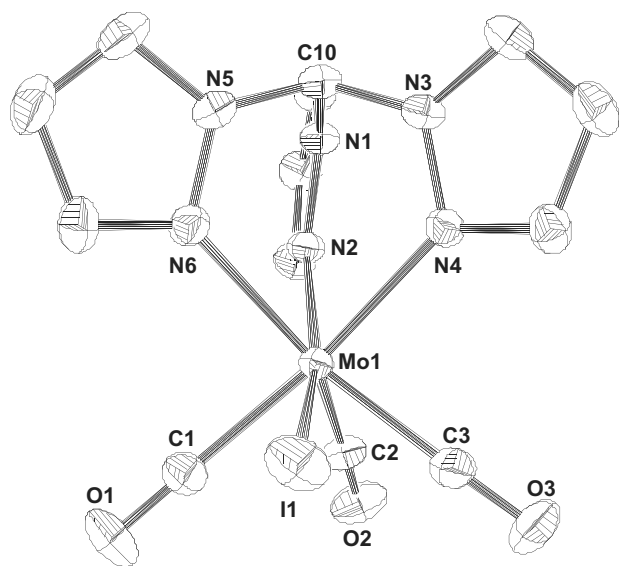


Fig. 4. Structure of the cation of $[\text{HC}(\text{pz})_3\text{Mo}(\text{CO})_3\text{I}]^+$ (**8a**), selected bond lengths (pm) and angles ($^\circ$): Mo1–C1 199.6(3), Mo1–C2 197.5(3), Mo1–C3 198.6(3), Mo1–I1 282.81(4), Mo1–N2 223.2(2), Mo1–N4 223.3(2), Mo1–N6 223.1(2), C1–O1 113.7(4), C2–O2 114.5(5), C3–O3 114.2(4), N1–N2 136.2(3), N3–N4 135.7(3), N5–N6 136.6(3); Mo1–C1–O1 178.2(3), Mo1–C2–O2 178.5(3), Mo1–C3–O3 177.5(3), Mo1–N2–N1 120.20(17), Mo1–N4–N3 121.18(17), Mo1–N6–N5 120.67(17), I1–Mo1–C1 76.67(8), I1–Mo1–C2 124.17(8), I1–Mo1–C3 73.60(10), I1–Mo1–N2 159.52(6), I1–Mo1–N4 89.00(6), I1–Mo1–N6 84.90(6), C1–Mo1–N2 109.21(10), C1–Mo1–N4 162.63(11), C1–Mo1–N6 88.34(11), C2–Mo1–N2 76.04(10), C2–Mo1–N4 122.43(11), C2–Mo1–N6 139.72(11), C3–Mo1–N2 122.00(12), C3–Mo1–N4 81.61(11), C3–Mo1–N6 152.17(12).

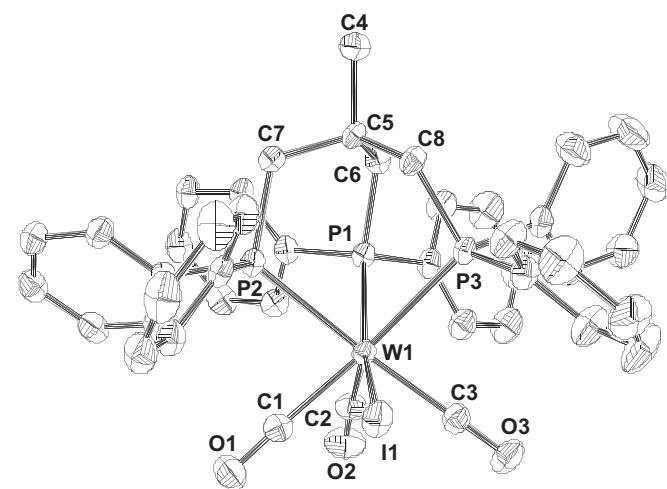
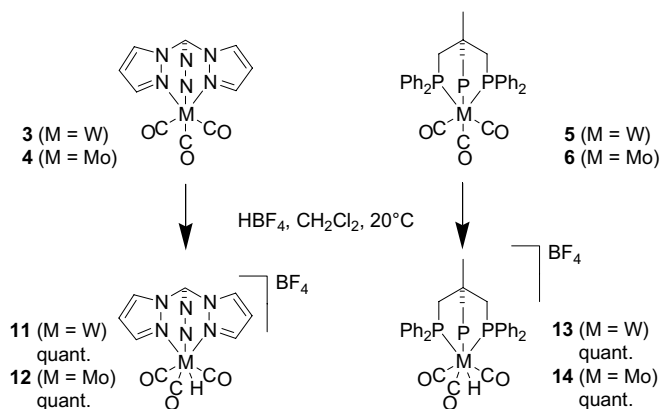


Fig. 5. Structure of the cation of $[\text{MeC}(\text{CH}_2\text{PPh}_2)_3\text{W}(\text{CO})_3\text{I}]^+$ (**9a**), selected bond lengths (pm) and angles ($^\circ$): W1–C1 202.3(4), W1–C2 197.7(4), W1–C3 201.5(4), W1–I1 284.35(3), W1–P1 255.74(9), W1–P2 260.44(9), W1–P3 263.48(9), C1–O1 113.6(4), C2–O2 114.7(5), C3–O3 113.3(4), P1–C6 184.6(4), P2–C7 184.5(3), P3–C8 181.9(3); W1–C1–O1 177.7(4), W1–C2–O2 172.7(3), W1–C3–O3 179.8(3), W1–P1–C6 112.59(11), W1–P2–C7 115.13(11), W1–P3–C8 107.63(12), I1–W1–C1 71.93(11), I1–W1–C2 126.84(11), I1–W1–C3 76.59(10), I1–W1–P1 157.17(2), I1–W1–P2 89.65(2), I1–W1–P3 83.04(2), C1–W1–P1 123.38(11), C1–W1–P2 78.29(11), C1–W1–P3 151.88(11), C2–W1–P1 75.93(11), C2–W1–P2 118.75(12), C2–W1–P3 135.77(11), C3–W1–P1 111.91(10), C3–W1–P2 164.57(11), C3–W1–P3 82.32(11).



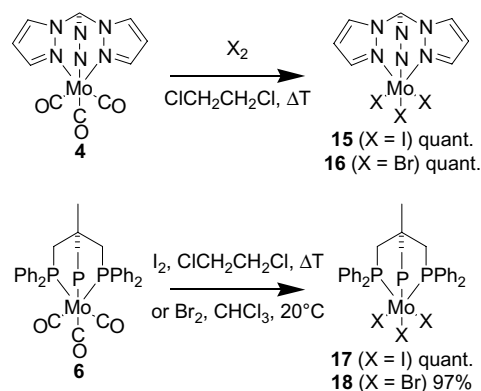
Equation 3. Oxidative addition of HBF_4 .

2.8. Oxidative decarbonylation

The reaction of $[\text{MeC}(\text{CH}_2\text{PPh}_2)_3\text{Mo}(\text{CO})_3]$ (**6**) with Br_2 proceeds differently at 20°C . After the addition of one equivalent Br_2 , a 1:1 mixture of **6** and $[\text{MeC}(\text{CH}_2\text{PPh}_2)_3\text{Mo}(\text{CO})_3\text{Br}]\text{Br}_3$ is observed by IR spectroscopy. However, addition of a second equivalent Br_2 results in a darkening of the reaction mixture, followed by gas evolution. The isolated solid is CO free by IR spectroscopy.

CO free complexes are also isolated when $[\text{LMo}(\text{CO})_3]$ (**4** and **6**) is heated with two equivalents of I_2 or Br_2 in dichloroethane. Characterization of the isolated yellow to dark brown solids is difficult, since no NMR signal is detected. In addition with the missing CO stretching frequency, it is assumed that complete decarbonylation to the corresponding paramagnetic Mo(III) complexes has occurred. This assumption is supported further by mass spectroscopy (Equation 4).

Efforts to isolate any Mo(II) intermediate of the type $[\text{LMo}(\text{CO})_2(\text{X})_2]$ were unsuccessful. The same is true for the more stable tungsten complexes. Until now, complexes $[\text{HC}(\text{pz})_3\text{M}(\text{CO})_3\text{X}]\text{X}$ (**7a, b, 8a, b**) could not be selectively decarbonylated, neither by heating in dichloroethane, acetonitrile or acetone, nor by the reaction of $[\text{LM}(\text{CO})_3]$ (**3–6**)



Equation 4. Oxidative decarbonylation of **4** and **6**.

with one equivalent of halogen under reflux in dichloromethane or acetonitrile.

3. Discussion

All tricarbonyl complexes **3–6** react smoothly with I_2 , Br_2 or HBF_4 at $20^\circ C$ to form seven-coordinated M(II) complexes except **6**, which reacts with Br_2 to form a CO-free compound. While the iodo complexes are usually air-stable, the bromo derivatives and the hydride complexes tend to decompose in air or under inert gas in solution. The addition of the halogen atoms on the metal is unambiguous according to the X-ray structure analysis. Although no crystals suitable for X-ray determination could be obtained from the hydrido complexes, the spectroscopic data of all oxidative addition products show similar features. The solution IR spectra of all compounds exhibit the typical pattern for seven-coordinated tricarbonyl complexes. The decrease in the CO values in the order $Br > I > H$ for all complexes reflects the decrease in relative electronegativity along the series Br, I, and H, and has already been observed for similar systems [22–25] (see Table 1).

Compared to their Tp or Tp* analogues [1,22,25–27], the $HC(pz)_3$ complexes show CO stretching frequencies which are between 10 and 25 cm^{-1} higher, due to the overall positive charge of the complexes. But even if neutral tripod nitrogen donor complexes like 1,4,7-triazacyclononane [23] or 1,3,5-triazacyclohexane [24] are taken into account, the stretching frequencies of the $HC(pz)_3$ complexes are still higher.

The solution IR spectra suggest a 4:3 piano stool or a 3:3:1 structure with C_S symmetry [24]. This would imply different sets of pyrazole protons and carbons as well as CO carbons in the 1H and ^{13}C NMR spectra. Since this is not the case, the complexes are fluxional in solution on the NMR time scale at room temperature and down to $-60^\circ C$ (Scheme 1).

An interesting feature of the complexes $[HC(pz)_3M(CO)_3X]X$ (**7a**, **b**, **8a**, **b**) is the downfield shift of the $HC(pz)_3$ proton in the 1H NMR spectrum. In all four complexes, this proton is found in the region between 11.5 and

13.0 ppm, with $[HC(pz)_3W(CO)_3Br]Br$ (**7b**) having the farthest downfield signal at 13.09 ppm. This is an additional 4–5 ppm compared to the free ligand. Since the six-coordinated, cationic complexes $[HC(pz)_3M(CO)_2(NO)]BF_4$ do not show such an extreme shift (9.86 for $M = W$ and 9.77 for $M = Mo$, respectively) [16,28], the origin of this spectroscopic feature must be the oxidation state and/or the seven-coordination of the metal. Since the Tp B–H proton is usually too broad to be observed, a comparison between the two ligands cannot be drawn properly in this case.

For the hydrido complexes $[HC(pz)_3M(CO)_3H]BF_4$ ($M = W$ **11**, Mo **12**), the signal for the M–H proton is found upfield at -2.50 (**11**) and -3.12 (**12**) ppm. The $^1J_{W,H}$ coupling constant of 10.4 Hz is additional proof for the addition of the proton to the metal. The small coupling constant as well as the chemical shifts are approximately the same as for $[TpM(CO)_3H]$ [22,26], while in $[(t-Bu_3tach)M(CO)_3H](CF_3SO_3)$ [24], the M–H proton is found even more upfield, and the $^1J_{W,H}$ coupling constant being nearly twice as big, underscoring the close relationship between Tp and $HC(pz)_3$ as ligands (Table 2).

The seven-coordinated complexes $[MeC(CH_2PPh_2)_3M(CO)_3X]^+$ show similar pattern in IR- and NMR spectroscopy. Their fluxionality can be observed even better. Since only a single resonance is found in the ^{31}P NMR spectra for all three phosphorus atoms, the approximate C_S symmetry in the crystal structure of **9a** is not a fixed structure in solution. Moreover, the methyl protons for all $MeC(CH_2PPh_2)_3$ complexes are split into quartets with a $^4J_{P,H}$ coupling constant of 3.0–3.2 Hz, indicating again that the phosphorus atoms are isochronous within the NMR time scale. That the observed coupling is indeed due to the phosphorus atoms was checked by a ^{31}P decoupled 1H NMR spectrum, in which the methyl protons were detected as a singlet. The hydride signals in $[MeC(CH_2PPh_2)_3M(CO)_3H]BF_4$ ($M = W$ **13**, Mo **14**) are also split into quartets with a $^2J_{P,H}$ coupling constant of 20.8 Hz and 20.0 Hz, respectively. The $^1J_{W,H}$ coupling constant in **13** is 12.7 Hz and thus slightly larger than in **11**. The resonances of the hydrides in **13** and **14** are shifted even more upfield (-4.62 and -4.20 ppm). Compared to $[HC(pz)_3M(CO)_3H]BF_4$ (**11**, **12**), the hydrides in **13** and **14** are more acidic: Weak bases such as THF, acetone and even diethyl ether are able to deprotonate the complexes.

It should be noted that for all hydrido complexes **11–14**, a single CO signal could be detected in the ^{13}C NMR spectra. This points to either a very small deviation from C_3 symmetry for **11–14** or to an even faster exchange process, both due to the small size of the hydrido ligand. In $[Tp^*W(CO)_3H]$, the deviation is large enough to render the three CO groups anisochronous [26], therefore a fast exchange process should be responsible for the single CO signal. The observed chemical shift between 206 and 220 ppm is typical for such complexes and has *inter alia* been found also for the CO groups of $[(t-Bu_3tach)M(CO)_3H](CF_3SO_3)$ [24].

Table 1
Characteristic spectroscopic data of the halogen complexes **7a–10a**

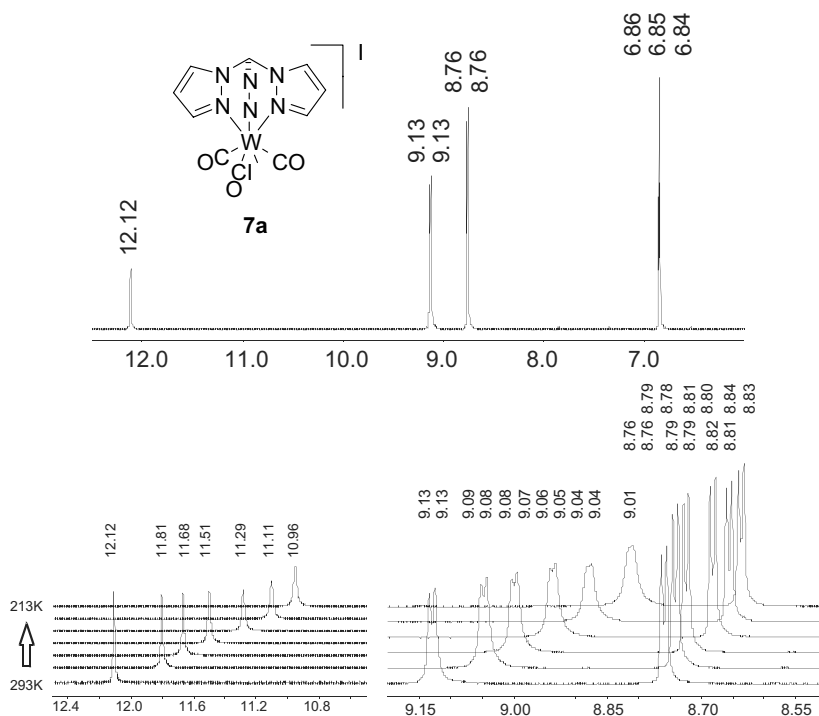
Complex	ν (CO) [cm^{-1}] ^a	$HC(pz)_3$ [ppm] ^c	$MeC(CH_2PPh_2)_3$ [ppm] ^d
7a	2036, 1960, 1927	12.38	
7b	2046, 1967, 1926	13.09	
8a	2045, 1979, 1948	11.73	
8b	2057, 1989, 1948	12.57	
9a	2030, 1973, 1928		$-23.5, ^1J_{W,P} = 157\text{ Hz}$
9b	2043, 1981, 1928 ^b		$-14.2, ^1J_{W,P} = 157\text{ Hz}$
10a	2043, 1973, 1920		-31.6

^a In CH_2Cl_2 .

^b Shoulder at 1904.

^c In d_6 -acetone.

^d In CD_2Cl_2 .

Scheme 1. Temperature dependent ^1H NMR spectra of **7a**.

The dicarbonyl complexes $[\text{MeC}(\text{CH}_2\text{PPh}_2)_3\text{M}(\text{CO})_2\text{X}_2]$ have been obtained recently by a different approach [29], and $[\text{TpM}(\text{CO})_3\text{X}]$ easily lose one CO group by gentle heating to form the 16 electron complexes $[\text{TpM}(\text{CO})_2\text{X}]$ [25,27]. Therefore, efforts were made to cleave a CO group thermally to form neutral dihalogen complexes $[\text{L}_3\text{M}(\text{CO})_2\text{X}_2]$. However, these attempts were unsuccessful so far. While $[\text{HC}(\text{pz})_3\text{M}(\text{CO})_3\text{X}]$ could be reisolated even after refluxing for several hours in dichloroethane, $[\text{MeC}(\text{CH}_2\text{PPh}_2)_3\text{M}(\text{CO})_3\text{X}]$ slowly dehalogenated and decomposed upon heating.

Complete oxidative decarbonylation, as observed by Enemark and coworkers for $[\text{HC}(3,5\text{-Mepz})_3\text{Mo}(\text{CO})_3]$ [30], seems to be possible for both Mo complexes $[\text{HC}(\text{pz})_3\text{Mo}(\text{CO})_3]$ (**4**) and $[\text{MeC}(\text{CH}_2\text{PPh}_2)_3\text{Mo}(\text{CO})_3]$ (**6**). This would explain the formation of a CO-free product if **6** is treated with two equivalents of Br_2 . This is the only example of the compounds investigated here where decarbonylation occurs at 20 °C. If **4** or **6** are refluxed in the presence of excess halogen in dichloroethane, gas evolution

indicates the loss of CO. Analysis of the solids obtained is difficult due to their low solubility, their paramagnetic nature, and the lack of IR active probes and the high percentage of halogen. However, IR spectroscopy indicates that the tripod ligands are still intact and coordinated. Mass spectroscopy confirms the integrity of the ligands and the presence of halogen.

The observation that **6** first forms $[\text{MeC}(\text{CH}_2\text{PPh}_2)_3\text{Mo}(\text{CO})_3\text{Br}]^+$ and later on decarbonylates suggest that the seven-coordinated molybdenum complexes isolated are intermediates in this reaction. With the starting complexes **4** and **6** being air-stable and easily accessible, this would be a new entrance to Mo(III) chemistry with facially coordinating tripod ligands. Work dealing with the topic of complete or partial oxidative decarbonylation is still in progress.

4. Conclusions

Adopting the high-yield synthesis of $[\text{HC}(\text{pz})_3\text{M}(\text{CO})_3]$ ($\text{M} = \text{W}$ **3**, Mo **4**) introduced by Trofimenko [16], $[\text{MeC}(\text{CH}_2\text{PPh}_2)_3\text{M}(\text{CO})_3]$ ($\text{M} = \text{W}$ **5**, Mo **6**) is prepared in higher yields and shorter reaction time. Careful oxidation using I_2 or Br_2 gives rise to seven-coordinated tricarbonyl complexes which show the typical fluxional behavior in solution, while in the solid state a pseudo C_3 symmetry and a 4:3 piano stool arrangement of the ligands around the metal is attained. Protonation of **3–6** occurs exclusively at the metal. In contrast to the well investigated Tp systems, neither $\text{HC}(\text{pz})_3$ nor $\text{MeC}(\text{CH}_2\text{PPh}_2)_3$ halogen complexes lose a CO group when heated. The molybde-

Table 2

Characteristic spectroscopic data of the hydrido complexes **11–14**

Complex	$\nu(\text{CO}) (\text{cm}^{-1})^{\text{a}}$	$MH (\text{ppm})^{\text{c}}$
11	2023, 1936, 1913	$-2.50, {}^1J_{\text{W,H}}=10.4 \text{ Hz}$
12	2030, 1947, 1926	-3.12
13	2027, 1956, 1933 ^b	$-4.62, {}^1J_{\text{W,H}}=12.7 \text{ Hz}, {}^2J_{\text{P,H}}=20.8 \text{ Hz}$
14	2032, 1962, 1937 ^b	$-4.20, {}^2J_{\text{P,H}}=20.0 \text{ Hz}$

^a In CH_2Cl_2 .^b Shoulder.^c In CD_2Cl_2 .

num complexes, however, can oxidatively be decarbonylated, which would open up a new way to Mo(III) chemistry.

5. Experimental

5.1. Reagents and general techniques

All experiments were carried out in Schlenk tubes under nitrogen using suitably purified solvents. IR: Bruker IFS 25. ^1H NMR: Bruker AMX 400, Joel JNM-LA 300, δ values relative to TMS. ^{13}C NMR: Bruker AMX 400, Joel JNM-LA 300, δ values relative to TMS. ^{31}P NMR: Bruker AMX 400, Joel JNM-LA 300, δ values relative to 85% H_3PO_4 . Mass spectroscopy: Finnigan MAT 90. Elemental analyses and melting points: Analytical Laboratory of the Institut für Anorganische Chemie. BF_4^- salts give low carbon values due to formation of fluorocarbon compounds which escape detection. The following starting materials were obtained as described in the literature: tris(pyrazolyl)methane (**1**) [18], 1,1,1-tris(diphenylphosphinomethyl)ethane (**2**) [19], $[\text{HC}(\text{pz})_3\text{W}(\text{CO})_3]$ (**3**) [16], $[\text{HC}(\text{pz})_3\text{Mo}(\text{CO})_3]$ (**4**) [16]. All other reagents were used as purchased.

5.2. Tricarbonyl complexes **5** and **6**

These complexes have been obtained previously in different two-step synthesis [20,21]. The following one-step synthesis gives higher yields. A suspension of $\text{M}(\text{CO})_6$ (W 4.00 g, Mo 3.00 g, 11.4 mmol) and $\text{MeC}(\text{CH}_2\text{PPh}_2)_3$ (7.00 g, 11.2 mmol) in DMF (40 mL) was refluxed for 16 h. Initially, the suspension turned into a clear yellow solution, which became dark brown towards the end. The reaction mixture was cooled to 20 °C, methanol (40 mL) was added, and the mixture was cooled further to 0 °C. The precipitate was filtered off, washed with methanol (5 mL portions) until the washing remained colorless, and dried under vacuum.

5.3. $[\text{MeC}(\text{CH}_2\text{PPh}_2)_3\text{W}(\text{CO})_3]$ (**5**)

Yield 8.00 g (8.96 mmol, 80%) white, crystalline solid. Analytical data were in agreement with values reported earlier [20].

5.4. $[\text{MeC}(\text{CH}_2\text{PPh}_2)_3\text{Mo}(\text{CO})_3]$ (**6**)

Yield 8.00 g (9.94 mmol, 89%) white, crystalline solid. Analytical data were in agreement with values reported earlier [21].

5.5. Halogen addition to $[\text{HC}(\text{pz})_3\text{M}(\text{CO})_3]$ (**3**) and (**4**)

The appropriate tricarbonyl complex (**3** 189 mg, **4** 154 mg, 0.391 mmol) was suspended in dichloromethane (5 mL). At 20 °C, one equivalent of elemental halogen (I_2

100 mg, Br_2 20.2 μL , 63 mg, 0.394 mmol) was added, resulting in a change of color of the reaction mixture. After 1 h, diethyl ether (15 mL) was added, the precipitate was filtered off, washed twice with diethyl ether (5 mL), and dried under vacuum.

5.6. $[\text{HC}(\text{pz})_3\text{W}(\text{CO})_3\text{I}]\text{I}$ (**7a**)

Yield 256 mg (0.348 mmol, 89%) orange powder, m.p. 105 °C (dec.). ^1H NMR (400 MHz, d_6 -acetone, 20 °C): δ = 6.85 (vt, $^3J_{\text{H,H}} = 2.6$ Hz, 3H, pyrazole-H4), 8.76 (dt, $^3J_{\text{H,H}} = 2.6$ Hz, $^4J_{\text{H,H}} = 0.7$ Hz, 3H, pyrazole-H3,5), 9.14 (dd, $^3J_{\text{H,H}} = 2.6$ Hz, $^4J_{\text{H,H}} = 0.7$ Hz, 3H, pyrazole-H3,5), 12.38 (s, 1H, $\text{HC}(\text{pz})_3$). ^{13}C NMR (100 MHz, d_6 -acetone, 20 °C) δ = 73.7 (s, $\text{HC}(\text{pz})_3$), 110.4 (s), 136.3 (s), 151.1 (s). IR (CH_2Cl_2): ν (CO) = 2036 (s) cm^{-1} , 1960 (s) cm^{-1} , 1927 (s) cm^{-1} . Anal. Calc.: $\text{C}_{13}\text{H}_{10}\text{I}_2\text{N}_6\text{O}_3\text{W}$ (735.91): C, 21.22; H, 1.37; N, 11.42. Found: C, 20.89; H, 1.45; N, 11.35%.

5.7. $[\text{HC}(\text{pz})_3\text{W}(\text{CO})_3\text{Br}]\text{Br}$ (**7b**)

Yield 226 mg (0.352 mmol, 90%) yellow powder, m.p. 80 °C (dec.). ^1H -NMR (400 MHz, d_6 -acetone, 20 °C): δ = 6.82 (vt, $^3J_{\text{H,H}} = 2.4$ Hz, 3H, pyrazole-H4), 8.63 (d, $^3J_{\text{H,H}} = 2.4$ Hz, 3H, pyrazole-H3,5), 9.13 (d, $^3J_{\text{H,H}} = 2.4$ Hz, 3H, pyrazole-H3,5), 13.09 (s, 1H, $\text{HC}(\text{pz})_3$). ^{13}C NMR (100 MHz, d_6 -acetone, 20 °C) δ = 73.7 (s, $\text{HC}(\text{pz})_3$), 110.3 (s), 137.2 (s, b), 150.2 (s). IR (CH_2Cl_2): ν (CO) = 2046 (s) cm^{-1} , 1967 (s) cm^{-1} , 1926 (m) cm^{-1} . Anal. Calc.: $\text{C}_{13}\text{H}_{10}\text{Br}_2\text{N}_6\text{O}_3\text{W}$ (641.91): C, 24.32; H, 1.57; N, 13.09. Found: C, 24.00; H, 1.76; N, 13.01%.

5.8. $[\text{HC}(\text{pz})_3\text{Mo}(\text{CO})_3\text{I}]\text{I}$ (**8a**)

Yield 212 mg (0.327 mmol, 84%) yellow-brown powder, m.p. 69 °C (dec.). ^1H NMR (400 MHz, d_6 -acetone, 20 °C): δ = 6.83 (vt, $^3J_{\text{H,H}} = 2.5$ Hz, 3H, pyrazole-H4), 8.71 (d, $^3J_{\text{H,H}} = 2.5$ Hz, 3 H, pyrazole-H3,5), 9.04 (d, $^3J_{\text{H,H}} = 2.5$ Hz, 3H, pyrazole-H3,5), 11.73 (s, 1H, $\text{HC}(\text{pz})_3$). ^{13}C NMR (100 MHz, d_6 -acetone, 20 °C) δ = 74.1 (s, $\text{HC}(\text{pz})_3$), 109.9 (s), 136.3 (s), 150.4 (s). IR (CH_2Cl_2): ν (CO) = 2045 (s) cm^{-1} , 1979 (s) cm^{-1} , 1948 (m) cm^{-1} . Anal. Calc. for $\text{C}_{13}\text{H}_{10}\text{I}_2\text{MoN}_6\text{O}_3$ (648.01): C, 24.10; H, 1.56; N, 12.97. Found: C, 24.32; H, 1.65; N, 12.69%.

5.9. $[\text{HC}(\text{pz})_3\text{Mo}(\text{CO})_3\text{Br}]\text{Br}$ (**8b**)

Yield 182 mg (0.329 mmol, 84%) brown powder, m.p. 63 °C (dec.). ^1H NMR (400 MHz, d_6 -acetone, 20 °C): δ = 6.80 (vt, $^3J_{\text{H,H}} = 2.0$ Hz, 3H, pyrazole-H4), 8.58 (d, $^3J_{\text{H,H}} = 2.0$ Hz, 3H, pyrazole-H3,5), 9.05 (d, $^3J_{\text{H,H}} = 2.0$ Hz, 3H, pyrazole-H3,5), 12.57 (s, b, 1 H, $\text{HC}(\text{pz})_3$). ^{13}C NMR (100 MHz, d_6 -acetone, 20 °C) δ = 109.9 (s), 149.5 (s); $\text{HC}(\text{pz})_3$ and one pyrazole-C not detected, IR (CH_2Cl_2): ν (CO) = 2057 (s) cm^{-1} , 1989 (s) cm^{-1} , 1948 (m) cm^{-1} . Anal. Calc. for $\text{C}_{13}\text{H}_{10}\text{Br}_2\text{MoN}_6\text{O}_3$ (554.01):

C, 28.18; H, 1.82; N, 15.17. Found: C, 27.86; H, 2.19; N, 15.38%.

5.10. Halogen addition to $[MeC(CH_2PPh_2)_3M(CO)_3]$ (**5**, **6**)

The appropriate tricarbonyl complex (**5** 175 mg, **6** 157 mg, 0.196 mmol) was suspended in dichloromethane (5 mL). At 20 °C, two equivalents of elemental halogen (I_2 100 mg, Br_2 20.2 μ L, 63 mg, 0.394 mmol) were added, resulting in a change of color of the reaction mixture. After 2 h, diethyl ether (10 mL) was added, the precipitate was filtered off, washed twice with diethyl ether (5 mL), and dried under vacuum.

5.11. $[MeC(CH_2PPh_2)_3W(CO)_3I]I_3$ (**9a**)

Yield 275 mg (0.196 mmol, quant.) orange-yellow powder, m.p. 108 °C (dec.). 1H NMR (400 MHz, CD_2Cl_2 , 20 °C): δ = 2.11 (q, $^4J_{P,H}$ = 3.1 Hz, 3H, CH_3), 3.06–3.12 (m, 6H, PCH_2), 7.13–7.35 (m, 30H, C_6H_5). ^{13}C NMR (100 MHz, CD_2Cl_2 , 20 °C) δ = 34.2–34.8 (m, PCH_2), 38.8–39.0 (m, CH_2CCH_3), 40.4–41.1 (m, CH_3), 129.0–133.0 (m, C_6H_5). ^{31}P NMR (162 MHz, CD_2Cl_2 , 20 °C): δ = –23.5 (s, $^1J_{W,P}$ = 157 Hz). IR (CH_2Cl_2): ν (CO) = 2030 (s) cm^{-1} , 1973 (s) cm^{-1} , 1928 (m) cm^{-1} . Anal. Calc. for $C_{44}H_{39}I_4O_3P_3W$ (1400.16): C, 37.74; H, 2.81. Found: C, 36.87; H, 2.92%.

5.12. $[MeC(CH_2PPh_2)_3W(CO)_3Br]Br_3$ (**9b**)

Yield 213 mg (0.176 mmol, 90%) orange-yellow powder, m.p. 72 °C (dec.). 1H NMR (300 MHz, CD_2Cl_2 , 20 °C): δ = 2.10–2.15 (m, 3H, CH_3), 3.09–3.14 (m, 6H, PCH_2), 7.11–7.34 (m, 30H, C_6H_5). ^{31}P NMR (121.5 MHz, CD_2Cl_2 , 20 °C) δ = –14.2 (s, $^1J_{W,P}$ = 157 Hz). IR (CH_2Cl_2): ν (CO) = 2043 (s) cm^{-1} , 1981 (s) cm^{-1} , 1928 (m) cm^{-1} , 1904 (sh) cm^{-1} . Anal. Calc. for $C_{44}H_{39}Br_4O_3P_3W$ (1212.16): C, 43.60; H, 3.24. Found: C, 43.86; H, 3.19%.

5.13. $[MeC(CH_2PPh_2)_3Mo(CO)_3I]I_3$ (**10a**)

Yield 257 mg (0.196 mmol, quant.) yellow-brown powder, m.p. 66 °C (dec.). 1H NMR (300 MHz, CD_2Cl_2 , 20 °C): δ = 2.37–2.62 (m, 6H, PCH_2), 2.99–3.25 (s, b, 3H, CH_3), 7.20–7.78 (m, 30H, C_6H_5). ^{31}P NMR (121.5 MHz, CD_2Cl_2 , 20 °C) δ = –31.6 (s, b). IR (CH_2Cl_2): ν (CO) = 2043 (s) cm^{-1} , 1973 (s) cm^{-1} , 1920 (s) cm^{-1} . Anal. Calc. for $C_{44}H_{39}I_4MoO_3P_3$ (1312.26): C, 40.27; H, 3.00. Found: C, 39.43; H, 3.16%.

5.14. Protonation of $[HC(pz)_3M(CO)_3]$ (**3,4**)

The appropriate tricarbonyl complex (**3** 189 mg, **4** 154 mg, 0.391 mmol) was suspended in dichloromethane (3 mL) at 20 °C. HBF_4 (100 μ L 54% in diethyl ether, 0.730 mmol) was added dropwise, resulting in a color

change of the reaction mixture. After 1 h, pentane (6 mL) was added, the precipitate was filtered off, washed twice with pentane (5 mL), and dried under vacuum.

5.15. $[HC(pz)_3W(CO)_3H]BF_4$ (**11**)

Yield 222 mg (0.390 mmol, quant.) blue powder, m.p. 138 °C (dec.). 1H NMR (400 MHz, CD_2Cl_2 , 20 °C): δ = –2.50 (s, $^1J_{W,H}$ = 10.4 Hz, 1H, WH), 6.56 (dd, $^3J_{H,H}$ = 2.4 Hz, $^3J_{H,H}$ = 2.4 Hz, 3H, *pyrazole-H4*), 8.24 (dt, $^3J_{H,H}$ = 2.4 Hz, $^4J_{H,H}$ = 0.7 Hz, 3H, *pyrazole-H3,5*), 8.45 (dd, $^3J_{H,H}$ = 2.4 Hz, $^4J_{H,H}$ = 0.6 Hz, 3H, *pyrazole-H3,5*), 9.57 (s, 1H, $HC(pz)_3$). ^{13}C NMR (100 MHz, CD_2Cl_2 , 20 °C) δ = 76.3 (s, $HC(pz)_3$), 109.7 (s), 135.3 (s), 149.6 (s), 214.3 (s, $^1J_{W,C}$ = 137 Hz, CO). IR (CH_2Cl_2): ν (CO) = 2023 (s) cm^{-1} , 1936 (s) cm^{-1} , 1913 (m) cm^{-1} . Anal. Calc. for $C_{13}H_{11}BF_4N_6O_3W$ (569.92): C, 27.40; H, 1.95; N, 14.75. Found: C, 23.29; H, 2.20; N, 13.27%.

5.16. $[HC(pz)_3Mo(CO)_3H]BF_4$ (**12**)

Yield 188 mg (0.390 mmol, quant.) brown powder, m.p. 124 °C (dec.). 1H NMR (400 MHz, CD_2Cl_2 , 20 °C): δ = –3.12 (s, 1H, MoH), 6.54 (vt, $^3J_{H,H}$ = 2.4 Hz, 3H, *pyrazole-H4*), 8.14 (d, $^3J_{H,H}$ = 2.4 Hz, 3H, *pyrazole-H3,5*), 8.42 (d, $^3J_{H,H}$ = 2.4 Hz, 3H, *pyrazole-H3,5*), 9.47 (s, 1H, $HC(pz)_3$). ^{13}C NMR (100 MHz, CD_2Cl_2 , 20 °C) δ = 75.8 (s, $HC(pz)_3$), 109.1 (s), 135.1 (s), 148.5 (s), 219.1 (s, CO). IR (CH_2Cl_2): ν (CO) = 2030 (s) cm^{-1} , 1947 (s) cm^{-1} , 1926 (m) cm^{-1} . Anal. Calc. for $C_{13}H_{11}BF_4MoN_6O_3$ (482.01): C, 32.39; H, 2.30; N, 17.44. Found: C, 28.65; H, 2.67; N, 16.60%.

5.17. Protonation of $[MeC(CH_2PPh_2)_3M(CO)_3]$ (**5,6**)

The appropriate tricarbonyl complex (**5** 175 mg, **6** 157 mg, 0.196 mmol) was suspended in dichloromethane (3 mL). At 20 °C, HBF_4 (50 μ L 54% in diethyl ether, 0.365 mmol) was added dropwise, resulting in clear solution. After 1 h, pentane (8 mL) was added, the precipitate was filtered off, washed twice with pentane (6 mL), and dried under vacuum.

5.18. $[MeC(CH_2PPh_2)_3W(CO)_3H]BF_4$ (**13**)

Yield 191 mg (0.195 mmol, quant.) off-white solid, m.p. 106 °C (dec.). 1H NMR (400 MHz, CD_2Cl_2 , 20 °C): δ = –4.62 (q, $^1J_{W,H}$ = 12.7 Hz, $^2J_{P,H}$ = 20.8 Hz, 1H, WH), 1.76 (q, $^4J_{P,H}$ = 3.2 Hz, 3H, CH_3), 2.67–2.73 (m, 6H, PCH_2), 7.05–7.43 (m, 30H, C_6H_5). ^{31}P NMR (162 MHz, CD_2Cl_2) δ = –9.4 (s, $^1J_{W,P}$ = 180 Hz). ^{13}C NMR (100 MHz, CD_2Cl_2 , 20 °C) δ = 32.5–32.9 (m, PCH_2), 38.5–38.6 (m, CH_2CCH_3), 39.2–39.3 (m, CH_3), 128.4–133.5 (m, C_6H_5), 206.7 (s, $^1J_{W,C}$ = 120 Hz, CO). IR (CH_2Cl_2): ν (CO) = 2027 (s) cm^{-1} , 1956 (s) cm^{-1} , 1933 (sh) cm^{-1} . Anal. Calc. for $C_{44}H_{40}BF_4O_3P_3W$ (980.35): C, 53.91; H, 4.11. Found: C, 45.85; H, 4.31%.

5.19. $[MeC(CH_2PPh_2)_3Mo(CO)_3H]BF_4$ (**14**)

Yield 174 mg (0.195 mmol, quant.) bright pink solid, m.p. 48 °C (dec.). 1H NMR (400 MHz, CD_2Cl_2 , 20 °C): $\delta = -4.20$ (q, $^2J_{P,H} = 20.0$ Hz, 1H, MoH), 1.76 (q, $^4J_{P,H} = 3.1$ Hz, 3H, CH_3), 2.60–2.66 (m, 6 H, PCH_2), 7.08–7.43 (m, 30H, C_6H_5). ^{31}P NMR (162 MHz, CD_2Cl_2 , 20 °C) $\delta = 8.3$ (s). ^{13}C NMR (100 MHz, CD_2Cl_2 , 20 °C) $\delta = 32.8$ – 33.2 (m, PCH_2), 36.7–36.8 (m, CH_2CCH_3), 38.9–39.2 (m, CH_3), 128.5–133.9 (m, C_6H_5), 214.6 (s, CO). IR (CH_2Cl_2): ν (CO) = 2032 (s) cm^{-1} , 1962 (s) cm^{-1} , 1937 (sh) cm^{-1} . Anal. Calc. for $C_{44}H_{40}BF_4MoO_3P_3$ (892.45): C, 59.22; H, 4.52. Found: C, 50.21; H, 4.62%.

5.20. Decarbonylation of $[HC(pz)_3Mo(CO)_3]$ (**4**)

$[HC(pz)_3Mo(CO)_3]$ (**4**) (154 mg, 0.391 mmol) was suspended in dichloroethane (8 mL). Two equivalents of halogen (I_2 200 mg, Br_2 40.4 μL , 126 mg, 0.788 mmol) were added and the resulting mixture refluxed for 2 h. After this time, no more gas evolution occurred and no more CO signals were detected by IR spectroscopy. Diethyl ether (10 mL) was added, the precipitate filtered off, washed twice with diethyl ether (5 mL) and dried under vacuum.

5.21. $[HC(pz)_3Mo(I)_3]$ (**15**)

Yield 270 mg (0.391 mmol, quant.) dark brown powder, m.p. 120 °C (dec.). $C_{10}H_{10}I_3MoN_6$ (690.88). MS (m/z): 281

(2) $[M^+ - 3I - N_2]$, 254 (77) $[I_2]^+$, 214 (5) $[HC(pz)_3]^+$, 147 (36) $[HC(pz)_2]^+$, 128 (90) $[HI]^+$, 80 (48) $[HC(pz)]^+$, 68 (100) $[pyrazole]^+$, 39 (8) $[C_3H_3]^+$.

5.22. $[HC(pz)_3Mo(Br)_3]$ (**16**)

Yield 214 mg (0.389 mmol, quant.) pink powder, m.p. 150 °C (dec.). $C_{10}H_{10}Br_3MoN_6$ (549.88). MS (m/z): 281 (4) $[M^+ - 3Br - N_2]$, 214 (7) $[HC(pz)_3]^+$, 147 (46) $[HC(pz)_2]^+$, 82 (50) $[HBr]^+$, 80 (88) $[HC(pz)]^+$ and $[HBr]^+$, 68 (100) $[pyrazole]^+$, 39 (8) $[C_3H_3]^+$.

5.23. $[MeC(CH_2PPh_2)_3Mo(I)_3]$ (**17**)

A suspension of $[MeC(CH_2PPh_2)_3Mo(CO)_3]$ (**6**) (157 mg, 0.195 mmol) and I_2 (200 mg, 0.788 mmol) in dichloroethane (8 mL) was refluxed for 2 h. After this time, no more gas evolution occurred and no more CO signals were detected by IR spectroscopy. Diethyl ether (20 mL) was added, the precipitate was filtered off, washed twice with diethyl ether, and dried under vacuum. Yield 213 mg (0.194 mmol, quant.) dark brown, m.p. 83 °C (dec.). $C_{41}H_{39}I_3MoP_3$ (1101.33).

5.24. $[MeC(CH_2PPh_2)_3Mo(Br)_3]$ (**18**)

$[MeC(CH_2PPh_2)_3Mo(CO)_3]$ (**6**) (2.00 g 2.45 mmol) was suspended in chloroform (20 mL). Br_2 (260 μL , 811 mg, 5.07 mmol) in chloroform (5 mL) was slowly added at

Table 3
Crystallographic parameters for the compounds **5**, **7a**, **7b**, **8a** and **9a**

	5	7a	7b × acetone	8a	9a × acetone
Empirical formula	$C_{44}H_{39}O_3P_3W$	$C_{13}H_{10}I_2N_6O_3W$	$C_{29}H_{260}Br_4N_{12}O_8W_2$	$C_{13}H_{10}I_2MoN_6O_3$	$C_{47}H_{45}I_4O_4P_3W$
Formula mass	892.51	735.92	1357.90	648.01	1458.19
Crystal colour/habit	Colorless block	Red block	Yellow plate	Red plate	Yellow plate
Crystal system	Hexagonal	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	R3	$P2_1/c$	$C2/c$	$P2_1/c$	$P\bar{1}$
a (Å)	17.8828(8)	14.7967(11)	28.252(3)	14.8429(12)	11.2687(9)
b (Å)	17.8828(8)	10.2086(8)	8.1760(7)	10.2615(8)	12.1769(9)
c (Å)	10.1843(9)	12.8024(10)	17.0343(14)	12.7685(11)	18.2463(14)
α (°)	90	90	90	90	97.054(2)
β (°)	90	100.4800(10)	91.265(2)	100.5710(10)	91.416(2)
γ (°)	120	90	90	90	95.895(2)
V (Å ³)	2820.5(3)	1901.6(3)	3933.8(6)	1911.8(3)	2469.9(3)
θ (°)	2.28–26.05	2.44–26.05	2.39–26.08	2.43–26.03	1.69–26.11
h	–22 to 22	–18 to 18	–34 to 34	–18 to 18	–13 to 138
k	–22 to 22	–12 to 12	–10 to 10	–12 to 12	–15 to 15
l	–12 to 12	–15 to 15	–21 to 21	–15 to 15	–22 to 22
Z	3	4	4	4	2
Crystal size (mm)	$0.32 \times 0.30 \times 0.25$	$0.33 \times 0.22 \times 0.22$	$0.32 \times 0.14 \times 0.06$	$0.37 \times 0.17 \times 0.10$	$0.31 \times 0.17 \times 0.03$
D_{calc} (g cm^{-3})	1.576	2.571	2.293	2.251	1.961
T (K)	173(2)	173(2)	173(2)	173(2)	173(2)
Reflections coll.	18386	38631	39889	38803	56778
Independent reflections	2486	3752	3883	3764	9788
Parameter	155	226	250	226	523
$R_1(I > 2\sigma(I))$	0.0155	0.0192	0.0504	0.0207	0.0262
R_1 (all data)	0.0155	0.0197	0.0531	0.0212	0.0301
$wR_2(I > 2\sigma(I))$	0.0385	0.0466	0.1196	0.0484	0.0616
wR_2 (all data)	0.0385	0.0469	0.1212	0.0486	0.0632
Difference in peak/hole (e Å ⁻³)	1.074/–0.221	0.642/–1.286	5.155/–4.583	0.605/–0.659	1.688/–0.542

20 °C. After approximately half of the Br₂ was added, the mixture turned dark and gas evolution was observed. After the mixture was stirred for 24 h, diethyl ether (25 mL) was added and the resulting suspension stirred for an additional hour. The supernatant liquid was decanted, the residue recrystallised from chloroform/diethyl ether, washed twice with diethyl ether (5 mL) and vacuum dried. Yield 2.31 g (2.41 mmol, 97%) yellow powder, m.p. 194 °C (dec.). Anal. Calc. for C₄₁H₃₉Br₃MoP₃ (960.32): C, 51.28; H, 4.09. Found: C, 51.62; H, 3.90%.

5.25. X-ray structure determinations

Single crystals of **5**, **7a**, **7b**, **8a** and **9a** were sealed to a glass fiber with frozen hydrocarbon oil. A Bruker Smart Apex CCD instrument with D8 goniometer was used for data collection (graphite monochromator, Mo K α radiation, $\lambda = 0.71073$ Å). The structures were solved using Patterson methods and refined with full-matrix least squares against F^2 (SHELXS-97) [31]. Hydrogen atoms were included in their calculated positions and refined in a riding model. The details of the measurements are summarized in Table 3.

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Appendix A. Supplementary data

CCDC 616688, 616686, 616685, 616687 and 616684 contain the supplementary crystallographic data for **5**, **7a**, **7b**, **8a** and **9a**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2007.02.021](https://doi.org/10.1016/j.jorganchem.2007.02.021).

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