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Metal-Template-Controlled Stabilization of β-Functionalized Isocyanides

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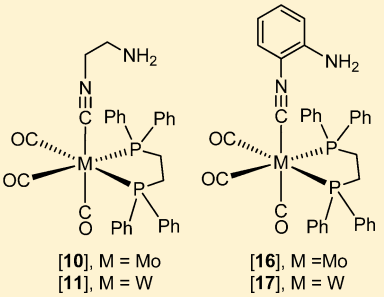
Supporting Information

ABSTRACT: Reaction of 2-azidoethyl isocyanide **1**, 2-azidophenyl isocyanide **2**, or 2-nitrophenyl isocyanide **3** with complexes $[Mo(CO)_3(dppe)(py)]$ [**4**] or $[W(CO)_3(dppe)(N{\equiv}CCH_3)]$ [**5**] yields the isocyanide complexes $[Mo(CO)_3(dppe)(C{\equiv}NR)]$ ([**6**]: C≡NR = **1**; [**12**]: C≡NR = **2**; [**13**]: C≡NR = **3**) and $[W(CO)_3(dppe)(C{\equiv}NR)]$ ([**7**]: C≡NR = **1**; [**14**]: C≡NR = **2**; [**15**]: C≡NR = **3**). Reduction of the nitro or azido groups attached to the isocyanide ligands by Zn/NH_4Cl (azidoethyl or azidophenyl isocyanides) or Raney-nickel/hydrazine hydrate (nitrophenyl isocyanide) yields exclusively the complexes bearing the 2-amino-functionalized isocyanides. The normally unstable 2-amino-functionalized isocyanides are stabilized by M→C≡NR back-bonding, which deactivates the isocyanide carbon atom for an intramolecular nucleophilic attack by the primary amine.



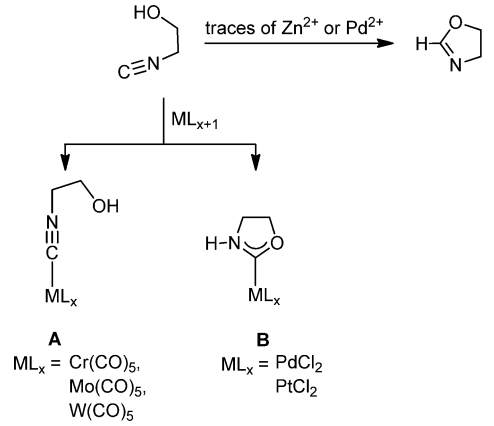
1. INTRODUCTION

Protic heterocarbene ligands can be generated at suitable metal templates from coordinated isocyanide ligands. Such coordinated isocyanides are attacked by protonated Lewis bases HX (X = OR, RNH) in a nucleophilic reaction that leads to carbene complexes.[1] A large number of complexes bearing acyclic carbenes[2] have been generated by this method.[3]

The use of complexes bearing functionalized isocyanides containing both the isocyanide group and the nucleophile in the same molecule gives access to complexes with heterocyclic carbene ligands via an intramolecular 1,2-addition across the C≡NR triple bond.[4] While the functionalized isocyanides can be generated in a template approach,[5] their direct use is much more facile.

Hydroxyalkyl isocyanides, such as 2-hydroxyethyl isocyanide, are stable molecules but are known to become activated on contact with selected metal ions where they isomerize to N,O-heterocycles. Even traces of Zn^{2+} or Pd^{2+} can initiate a vigorous exothermic reaction.[6] Fehlhammer et al. used this type of cyclization for the metal-template-controlled generation of NH,O-heterocarbene ligands (Scheme 1). The intramolecular cyclization reaction is strongly dependent on the template metal complex. At some zerovalent metal centers, such as $\{M(CO)_5\}$ (M = Cr, Mo, W), the isocyanide ligand coordinates to the metal atom to give complexes of type **A**. Here, the isocyanide ligand is not sufficiently activated for a subsequent cyclization reaction (free ligand: $\tilde{\nu}_{CN}$ 2153 cm^{-1}; $[Cr(CO)_5(CNCH_2CH_2OH]$: $\tilde{\nu}_{CN}$ 2178 cm^{-1}; $[Mo(CO)_5(CNCH_2CH_2OH]$: $\tilde{\nu}_{CN}$ 2164 cm^{-1}).[7] However, if the metal atom is electron deficient, like in the case of Pd^{2+} or Pt^{2+}, isocyanide complexes cannot be isolated and, instead,

Scheme 1. Reactions of 2-Hydroxyethyl Isocyanide with Selected Metal Complexes



complexes of type **B** bearing the oxazolidin-2-ylidenen ligand are formed by an intramolecular cyclization reaction.[8]

A substitution of the ethyl spacer in 2-hydroxyethyl isocyanide for a 1,2-phenyl group leads to 2-hydroxyphenyl isocyanide. This ligand, however, contains the isocyanide and the hydroxyl group in the same molecule, and these two groups are also arranged in one plane, facilitating an intramolecular cyclization. Consequently and contrary to 2-hydroxyethyl isocyanide, 2-hydroxyphenyl isocyanide is not stable in the free state but spontaneously cyclizes to yield benzoxazole even in the absence of any metal ions[9] (Scheme 2). The benzoxazole

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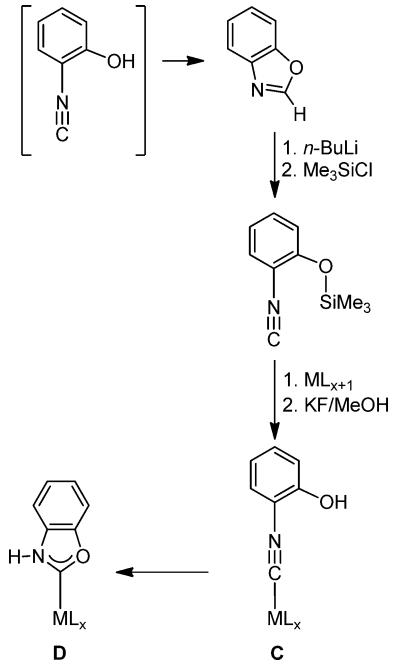
Scheme 2. Reactions of 2-Hydroxyphenyl Isocyanide

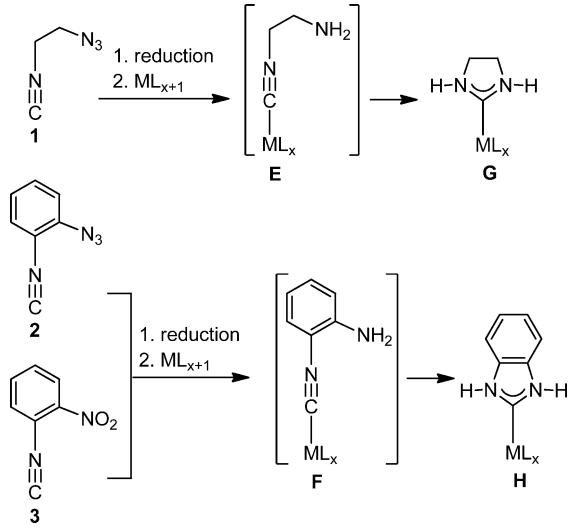


heterocycle opens up upon treatment with *n*-BuLi, and the isocyanide obtained in this way can be stabilized as 2-trimethylsiloxyphenyl isocyanide by reaction with trimethylsilyl chloride.[10] Coordination of trimethylsiloxyphenyl isocyanide to different metal complexes leads to isocyanide complexes, which, upon cleavage of the O−$SiMe_3$ bond, react to yield complexes with a 2-hydroxyphenyl isocyanide (**C**)[11] or a benzoxazolin-2-ylidene ligand (**D**,[12] Scheme 2). As in the case of the 2-hydroxyethyl isocyanide, the final outcome of the reaction is determined by the electronic situation at the complex fragment. Stabilization of the freely unstable 2-hydroxyphenyl isocyanide in complexes of type **C** has been achieved at electron-rich complex fragments that are engaged in strong M→C≡NR back-bonding, thereby deactivating the isocyanide for an intramolecular nucleophilic attack by the hydroxyl group. Occasionally, an equilibrium between complexes of types **C** and **D** has been observed.[13]

The amine-substituted derivatives of 2-hydroxyethyl isocyanide (2-aminoethyl isocyanide) and 2-hydroxyphenyl isocyanide (2-aminophenyl isocyanide) are not stable as free molecules and immediately cyclize to give, for example, benzimidazole. As in the case of 2-hydroxyphenyl isocyanide (Scheme 2), the *β*-amino-substituted isocyanides can only be generated in a template-controlled approach at suitable metal centers. We have used 2-azidoethyl isocyanide **1**, 2-azidophenyl isocyanide **2**, and 2-nitrophenyl isocyanide **3** as synthons for 2-aminoethyl isocyanide and 2-aminophenyl isocyanide, respectively. Coordination of the isocyanides **1**−**3**, followed by reduction of the azido or nitro groups, leads to complexes bearing *β*-amino-functionalized isocyanides (**E**, **F**), which, in all cases described so far, are unstable and rapidly undergo an intramolecular cyclization reaction to give the complexes bearing saturated[14] (**G**) or benzannulated[15] NH,NH-NHC ligands (**H**).

We became interested in the intermediary complexes bearing the *β*-amino-functionalized isocyanides. In this contribution, we describe electron-rich complexes of types **E** and **F**, where enhanced M→C≡NR back-bonding from the metal atom to the isocyanide prevents the intramolecular cyclization and allows the characterization of complexes bearing the elusive *β*-amino functionalized isocyanide ligands Scheme 3). Such

Scheme 3. Reactions of *β*-Functionalized Ethyl and Phenyl Isocyanides



complexes have not been isolated so far, but some related *α*,*ω*-aminoalkyl isocyanides featuring a $(CH_2)_3$ or $(CH_2)_4$ alkyl chain between the amine and the isocyanide groups also do not cyclize to the six- or seven-membered NHCs at the template metal studied.[16] Previous reports on the isolation of the {$Cr(CO)_5$}complex of *β*-aminophenyl isocyanide[17] must be taken with caution as this complex has been shown unequivocally by X-ray diffraction to react with cyclization of the *β*-aminophenyl isocyanide to give the complex with an NH,NH-NHC ligand.[15a]

2. RESULTS AND DISCUSSION

The stabilization of 2-hydroxyalkyl[7] and -phenyl isocyanides[11,13] has been achieved at electron-rich transition-metal complex fragments where the M→C≡NR back-bonding prevents the intramolecular nucleophilic attack of the hydroxyl group at the isocyanide carbon atom. The analogous stabilization of 2-aminoethyl or -phenyl isocyanides has not been demonstrated yet, which is most likely due to the enhanced nucleophilicity of the amino group in comparison to the hydroxyl group. We have tried to identify such metal templates that would provide enough electron density and M→C≡NR back-bonding to stabilize the reactive *β*-amino-functionalized isocyanide ligands. Since even complex fragments of zerovalent transition metals, such as {$M(CO)_5$} (M = Cr, Mo, W), allowed the cyclization of coordinated 2-aminoethyl isocyanide[14] and 2-aminophenyl isocyanide,[15] we envisaged that the substitution of some of the *π*-acceptor carbonyl ligands for strong *σ*-donor and weak *π*-acceptor ligands might change the electronic situation at the metal atom sufficiently to allow the stabilization of coordinated *β*-amino-functionalized isocyanides. The chelating diphosphine ligand dppe was selected for this task.

We have prepared complex [$Mo(CO)_3$(dppe)(py)] [**4**] from [$Mo(CO)_3(py)_3$][18] and dppe. This complex was not purified but used for subsequent reactions as obtained. Complex [$W(CO)_3$ (dppe)($NCCH_3$)] [**5**] was prepared from [W-

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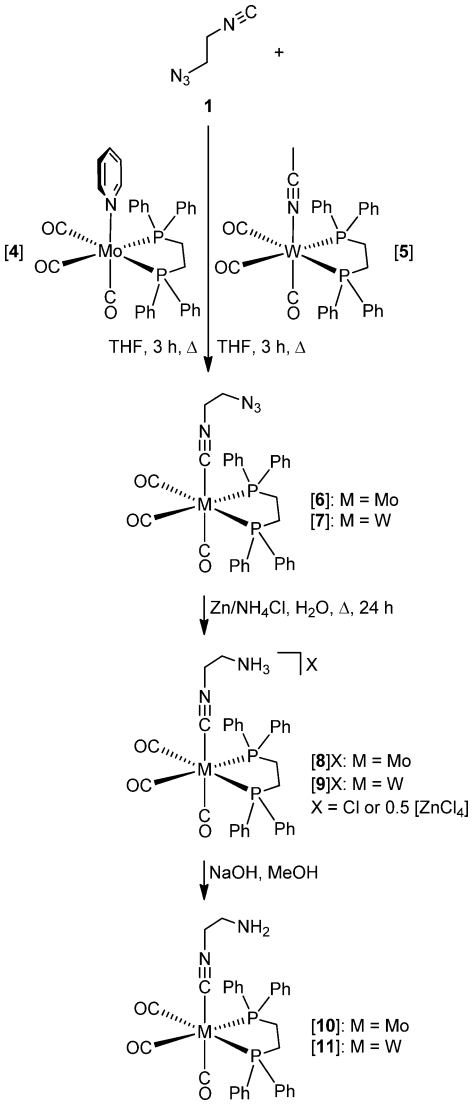
$(CO)_6$] and dppe in acetonitrile and isolated as described.[19] Both complexes [**4**] and [**5**] react with 2-azidoethyl isocyanide **1**[14b,d] with substitution of the nitrogen donor to yield the isocyanide complexes [**6**] and [**7**] (Scheme 4). The isocyanide

Scheme 4. Stabilization of 2-Aminoethyl Isocyanide at Metal Templates



C≡NR resonances in the $^{13}C\{^1H\}$ NMR spectra were observed at δ = 167.4 ppm for [**6**] and at δ = 159.5 ppm for [**7**]. The resonance for [**6**] shows $^2J_{PC(isocyanide)}$ coupling, but lacks the $^1J_{CN}$ coupling found for the free ligand **1**[14b] and for related aliphatic isocyanides.[20] The lack of $^1J_{CN}$ coupling can be taken as an indication for metal coordination of the isocyanide ligand.[20] The isocyanide stretching vibration for [**6**] was observed at $\tilde{\nu}$ = 2135 cm^{-1} and at $\tilde{\nu}$ = 2129 cm^{-1} for [**7**]. These values represent a shift of 17 and 23 cm^{-1}, respectively, to lower wavenumbers upon metal coordination compared to the free ligand **1** ($\tilde{\nu}$ = 2152 cm^{-1}).[14b] The shift to lower wavenumbers indicates the desired strong back-bonding from the metal atom to the isocyanide ligand and a weakening of the C≡NR bond of the isocyanide. It was hoped for that the enhanced M→C≡NR back-bonding in [**6**] and [**7**] proved sufficient to prevent an intramolecular nucleophilic attack after reduction of the azido function of the ligand to a primary amine.

The formation of the molybdenum complex [**6**] was corroborated by an X-ray diffraction analysis (Figure 1, top).

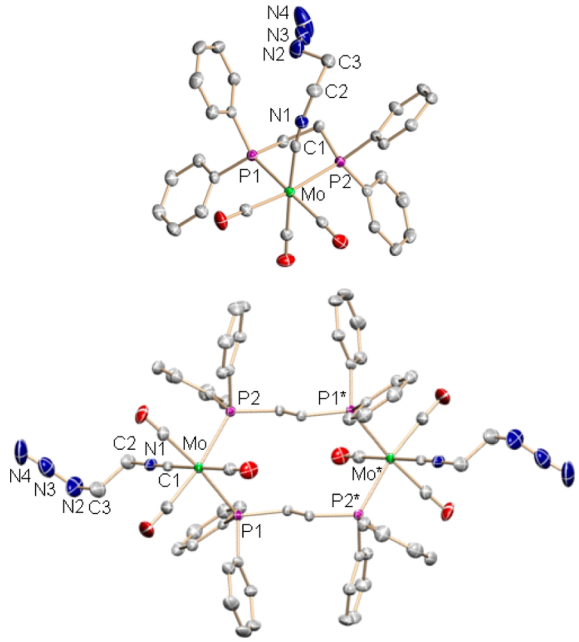


Figure 1. Molecular structures of [**6**] (top) and $[\mathbf{6}]_2$ in $[\mathbf{6}]_2 \cdot 2CH_2Cl_2$ (bottom, 50% displacement ellipsoids, hydrogen atoms and solvent molecules have been omitted; complex $[\mathbf{6}]_2$ resides on a crystallographic inversion center). Selected bond lengths (Å) and angles (deg) for [**6**], $[[\mathbf{6}]_2 \cdot 2CH_2Cl_2]$: Mo−C1 2.140(2) [2.125(3)], C1−N1 1.163(2) [1.151(3)], N1−C2 1.434(2) [1.439(3)], C3−N2 1.476(3) [1.464(4)], N2−N3 1.210(3) [1.267(4)], N3−N4 1.333(3) [1.089(4)]; Mo−C1−N1 174.55(15) [178.5(2)], C1−N1−C2 169.7(2) [177.7(3)], N2−N3−N4 171.1(3) [170.4(4)].

The structure analysis revealed the expected slightly bent arrangement of the isocyanide group (angle C1−N1−C2 169.7(2)°), which is most likely caused by M→C≡NR back-bonding.[1] The N2−N3−N4 angle of the azide group measures 171.1(3)°.

Beside the expected mononuclear complex [**6**], the dinuclear complex $[\mathbf{6}]_2$ was found as a side product upon crystallization of [**6**]. The X-ray diffraction analysis of $[\mathbf{6}]_2 \cdot 2CH_2Cl_2$ revealed the unexpected coordination of dppe as a bridging ligand. Normally, the coordination chemistry of dppe is dominated by the formation of stable complexes featuring five-membered chelate rings that are thermodynamically favored in comparison to a bridging coordination mode. In fact, there is only one report describing the M(μ-dppe)$_2$M structural motif. Homo- and heterobimetallic complexes of the type [$(CO)_4$M(μ-dppe)M′$(CO)_4$] (M, M′ = Cr, Mo, W) have been prepared in a base-catalyzed template synthesis starting from equimolar amounts of complexes of types [$M(CO)_4(PPh_2H)_2$] and [$M(CO)_4(PPh_2CH{=}CH_2)_2$].[21] In the $^{31}P\{^1H\}$ NMR spectra, the resonance for the dinuclear complex [$(CO)_4$Mo(μ-dppe)$_2$Mo$(CO)_4$] (s, δ = 29.6 ppm) differs significantly from that for the mononuclear chelate complex [$Mo(CO)_4$(dppe)] (s, δ = 55.4 ppm). Since the $^{31}P\{^1H\}$ NMR spectrum of [**6**] revealed only one resonance in the range typical for mononuclear complexes (δ = 55.48 ppm), we assume that $[\mathbf{6}]_2$ is obtained as a side product during the crystallization of [**6**]. Equivalent metric parameters are similar for [**6**] and $[\mathbf{6}]_2$.

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Next, the azido functions in [**6**] and [**7**] were reduced to primary amines (Scheme 4). Previous studies had shown that a mixture of zinc powder, ammonium chloride, and water in methanol is particularly useful for this reduction and does not interfere with the central metal atom.[15e,22] The reduction yielded the ammonium salts [**8**]X and [**9**]X (X^- = Cl^-, $0.5[ZnCl_4]^{2-}$) as isolable materials, containing a mixture of two different counterions. Mass spectrometry (ESI and MALDI, negative ions) of these compounds provided evidence for the presence of both, chloride and tetrachlorozincate counterions. The amount of these anions could not be determined, allowing only a rough estimate of the yield in this reaction step.

Treatment of complexes [**8**]X and [**9**]X with sodium hydroxide in methanol finally yielded complexes [**10**] and [**11**] bearing the 2-aminoethyl isocyanide ligand. No indication for the formation of an equilibrium between the isocyanide and the NHC complex was observed. Complexes [**10**] and [**11**] are the first examples for which the normally favored intramolecular cyclization of 2-aminoethyl isocyanide to the NH,NH-NHC ligand has been suppressed. Instead, the reactive isocyanides are stabilized at the metal template.

Complexes [**10**] and [**11**] have been characterized spectroscopically. The IR spectra show no absorptions due to the N_3 group anymore, while the wavenumbers for the C≡NR stretching vibrations have been detected at $\tilde{\nu}$ = 2133 cm^{-1} (for [**10**]) and $\tilde{\nu}$ = 2126 cm^{-1} (for [**11**]). These absorptions are shifted only marginally toward lower wavenumbers in comparison to the azide complexes [**6**] and [**7**]. In addition, new absorptions at $\tilde{\nu}$ = 3441 and 3396 cm^{-1} (for [**10**]) and $\tilde{\nu}$ = 3447 and 3363 cm^{-1} (for [**11**]) were observed, which have been assigned to the NH_2 group. The $^{13}C\{^1H\}$ NMR spectra exhibit the resonance for the isocyanide carbon atom at δ = 164.0 (for [**10**]) and at δ = 156.0 ppm (for [**11**]), respectively. The ^1H NMR spectra feature the resonances for the amine protons at δ = 0.45 ppm for [**10**] and at δ = 0.61 ppm for [**11**]. These signals are shifted slightly high field in comparison to free aliphatic primary amines.[23]

Formation of the 2-aminoethyl isocyanide complex [**10**] was confirmed by an X-ray diffraction analysis. Suitable single crystals were obtained by slow diffusion of diethyl ether into a saturated solution of [**10**] in dichloromethane. The molecular structure of [**10**] is depicted in Figure 2 (the ethyl spacer between the C≡N and NH_2 groups is disordered over two position, only one of which is depicted). The isocyanide ligand features no unusual metric parameters. The C1−N1−C2 bond angle (171.4(4°) deviates significantly from linearity, as would be expected for an isocyanide ligand stabilized by Mo→C≡NR back-bonding. The back-bonding to the isocyanide also manifests itself in two short Mo−CO (*trans* to P, 1.976(2) and 1.979(2) Å) and a long Mo−CO (*trans* to C≡NR, 1.992(2) Å) bond.

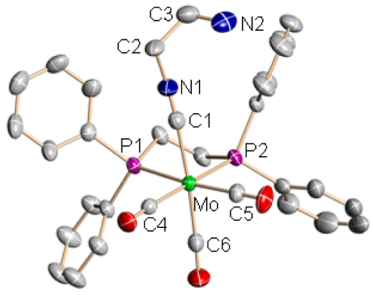
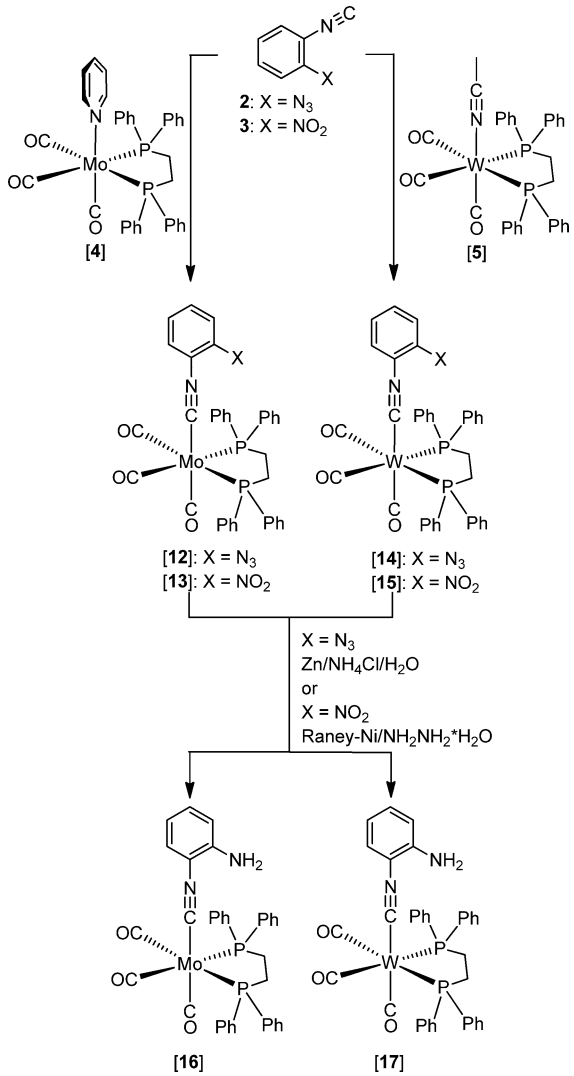


Figure 2. Molecular structure of [**10**] (50% displacement ellipsoids; hydrogen atoms have been omitted). Selected bond lengths (Å) and angles (deg): Mo−C1 2.157(2), Mo−C4 1.976(2), Mo−C5 1.979(2), Mo−C6 1.992(2), C1−N1 1.139(3); Mo−C1−N1 176.0(2), C1−N1−C2 171.4(4).

Next, we studied the complexes containing the phenyl isocyanides **2** and **3** (Scheme 5). Reduction of the azido or nitro functions of the coordinated isocyanide ligands would lead to complexes bearing the 2-aminophenyl isocyanide, a ligand not known in the free state as it immediately cyclizes to yield benzimidazole. The reaction of 2-azidophenyl isocyanide **2** with complexes [**4**] and [**5**] yielded the isocyanide complexes [**12**] and [**14**], respectively. These complexes, however, are not stable enough to be isolated in a pure form. Generally, aromatic isocyanides are less nucleophilic than their aliphatic analogues, which might contribute to the instability of complexes [**12**] and [**14**]. The crude reaction products were, therefore, used for the subsequent reduction of the azido function. The related complexes bearing the 2-nitrophenyl isocyanide [**13**] and [**15**] are more stable and were isolated and spectroscopically characterized.

Scheme 5. Stabilization of 2-Aminophenyl Isocyanide at Metal Templates



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Whereas the ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of [**13**] and [**15**] differ only slightly, the resonances in the $^{31}P\{^{1}H\}$ NMR spectra vary significantly ([**13**]: δ = 56.45 ppm; [**15**]: δ = 40.60 ppm, $^{1}J_{PW}$ = 225.3 Hz). The absorption for the C≡NR stretching vibration was detected at $\tilde{\nu}$ = 2063 cm^{-1} for complex [**13**] and at $\tilde{\nu}$ = 2059 cm^{-1} for [**15**]. These values and the shift to lower wavenumbers compared to the free 2-nitrophenyl isocyanide **3**[15b] ($\tilde{\nu}$ = 2129 cm^{-1}) by $\Delta\tilde{\nu} \approx$ 70 cm^{-1} indicate that coordination of **3** in the electron-rich complexes [**13**] and [**15**] leads to enhanced M→C≡NR back-bonding and concurrent deactivation of the isocyanide for a nucleophilic attack. The drop in the wavenumber upon metal coordination is even stronger than that observed for the similar complexes [**6**] and [**7**] bearing the aliphatic 2-azidoethyl isocyanide ligand ($\Delta\tilde{\nu} \approx$ 20 cm^{-1}), which can be attributed to the generally better π-acceptor properties of aromatic isocyanides.

In addition, complexes [**13**] and [**15**] were characterized by X-ray diffraction studies. Suitable crystals of [**13**]·THF and [**15**]·Et_2O were obtained by slow evaporation of the solvent from solutions of the complexes in THF and Et_2O, respectively. The molecular structures of [**13**] and [**15**] are depicted in Figure 3. The molecular structure determinations confirmed

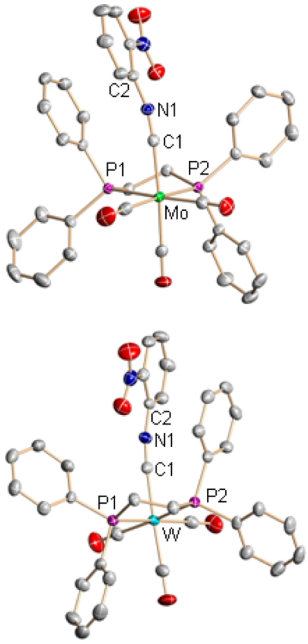

Figure 3. Molecular structure of [**13**] in [**13**]·THF (top) and [**15**] in [**15**]·Et_2O (bottom, 50% displacement ellipsoids; hydrogen atoms have been omitted). Selected bond lengths (Å) and angles (deg) for [**13**], [**15**]: M−C1 2.098(2) [2.080(3)], C1−N1 1.171(2) [1.173(4)]; M−C1−N1 174.3(2) [175.8(3)], C1−N1−C2 164.7(2) [167.1(3)].

the expected connectivity. The change from molybdenum in [**13**] to tungsten [**15**] does not lead to significantly different metric parameters. In comparison to the related, but less electron-rich complexes of the type [$M(CO)_5$(**3**)] (M = Mo, W),[15b] the enhanced back-bonding in [**13**] and [**15**] is reflected in a further reduction of the C1−N1−C2 angles to 164.7(2)° for [**13**] and 167.1(3)° for [**15**]. The enhanced ability of the metal centers in [**13**] and [**15**] to engage in M→C≡NR back-bonding also leads to a general shortening of the M−CO bonds compared with complexes of the type [$M(CO)_5$(**3**)]. Generally, the metric parameters involving the isocyanide ligands in [**13**] and [**15**] do not differ significantly from those observed in complexes of the type [$M(CO)_5$(**3**)], confirming previous observations that metric parameters associated with isocyanide ligands are less informative than spectroscopic data in the assessment of the bonding situation.[24]

Reduction of the functional groups of the isocyanide ligands in [**12**]−[**15**] was achieved with Zn/NH_4Cl/H_2O for the 2-azidophenyl isocyanide complexes or with Raney nickel/hydrazine hydrate for the 2-nitrophenyl isocyanide complexes. This led to complexes [**16**] and [**17**], respectively, bearing the 2-aminophenyl isocyanide ligand (Scheme 5). Clearly, the electronic situation and the M→C≡NR back-bonding in these complexes prevented the ubiquitous cyclization to the benzannulated NH,NH-NHC ligand.[15]

Complexes [**16**] and [**17**] were studied by NMR and IR spectroscopy. The IR spectra showed the isocyanide stretching vibrations at $\tilde{\nu}$ = 2097 cm^{-1} ([**16**]) or $\tilde{\nu}$ = 2093 cm^{-1} ([**17**]) in addition to two absorptions at high wavenumbers ([**16**]: $\tilde{\nu}$ = 3484 and 3394 cm^{-1}; [**17**]: $\tilde{\nu}$ = 3482 and 3389 cm^{-1}), which were assigned to the stretching vibrations of the NH_2 groups. The resonances for the isocyanide carbon atoms were found at δ = 177.1 ppm for [**16**] and at δ = 169.3 ppm for [**17**] (in [D_8]THF.

Single crystals of [**16**] and [**17**] were obtained by evaporation of the solvent from a saturated dichloromethane solution of [**16**] or a saturated THF solution of [**17**]. The molecular structures of [**16**] and [**17**] are depicted in Figure 4.

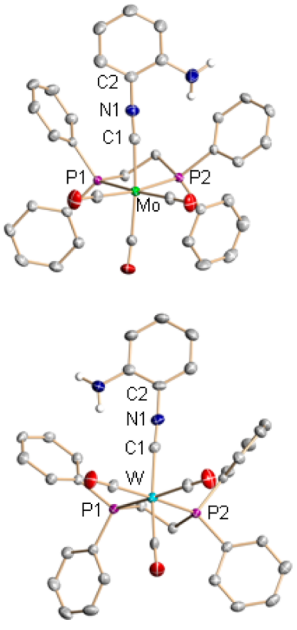

Figure 4. Molecular structures of [**16**] (top) and [**17**] (bottom, 50% displacement ellipsoids; hydrogen atoms, except for those bound to N2, have been omitted). Selected bond lengths (Å) and angles (deg) for [**16**], [**17**]: M−C1 2.129(2) [2.113(3)], C1−N1 1.161(3) [1.161(4)]; M−C1−N1 176.0(2) [176.4(3)], C1−N1−C2 176.5(2) [176.5(3)].

The most significant differences in the metric parameters of the 2-nitrophenyl isocyanide complexes [**13**] and [**15**] and the 2-aminophenyl isocyanide complexes [**16**] and [**17**] result from the reduction of the π-acceptor character of 2-aminophenyl isocyanide compared to 2-nitrophenyl isocyanide. As the isocyanide ligands in [**16**] and [**17**] are weaker π acids, the M−C≡NR bond lengths increase (for example, from 2.098(2)

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Table 1. IR Spectroscopic Data for Isocyanide Complexes

complex fragment	isocyanide ligand	compound	$\tilde{\nu}$ (NC) (cm^{-1})	k(NC) (Nm^{1-})	after reduction
$Mo(CO)_5$	$CNCH_2CH_2N_3$ **1**	[**18**]	2176	1803	ylidene
$Mo(CO)_3$(dppe)	$CNCH_2CH_2N_3$ **1**	[**6**]	2135	1736	isocyanide
$Mo(CO)_3$(dppe)	$CNCH_2CH_2NH_2$	[**10**]	2133	1733	
$Mo(CO)_3$(dppe)	$CNC_6H_4N_3$ **2**	[**12**]	2077	1643	isocyanide
$Mo(CO)_5$	$CNC_6H_4NO_2$ **3**	15b	2133	1733	ylidene
$Mo(CO)_3$(dppe)	$CNC_6H_4NO_2$ **3**	[**13**]	2063	1621	isocyanide
$Mo(CO)_3$(dppe)	$CNC_6H_4NH_2$	[**16**]	2097	1675	
$W(CO)_5$	$CNCH_2CH_2N_3$ **1**	14b	2187	1822	ylidene
$W(CO)_3$(dppe)	$CNCH_2CH_2N_3$ **1**	[7]	2129	1726	isocyanide
$W(CO)_3$(dppe)	$CNCH_2CH_2NH_2$	[**11**]	2126	1721	
$W(CO)_5$	$CNC_6H_4N_3$ **2**	15a	2141	1746	ylidene
$W(CO)_3$(dppe)	$CNC_6H_4N_3$ **2**	[**14**]	2075	1640	isocyanide
$W(CO)_5$	$CNC_6H_4NO_2$ **3**	15b	2134	1734	ylidene
$W(CO)_3$(dppe)	$CNC_6H_4NO_2$ **3**	[**15**]	2059	1615	isocyanide
$W(CO)_3$(dppe)	$CNC_6H_4NH_2$	[**17**]	2093	1668	

Å in [**13**] to 2.129(2) Å in [**16**]) and the isocyanide group becomes more linear (angle C1−N1−C2 164.7(2)° in [**13**] and 176.0(2)° in [**16**]).

Isocyanides act, similarly to CO, as σ-donor/π-acceptor ligands. The reactivity of a coordinated isocyanide ligand is significantly affected by the metal atom it coordinates to. This reactivity can be related to the IR absorption frequency or the force constants of the C≡NR bond.[4a,13a] The force constant can be directly correlated with the positive charge at the C≡N carbon atom and, therefore, to its sensibility for a nucleophilic attack. We have calculated the force constants for the isocyanides described in this contribution using the method of Cotton and Kraihanzel[25] with corrections for the mass difference between CO and CN (Table 1; complex [$Mo(CO)_5(C{\equiv}N{-}CH_2{-}CH_2{-}N_3)$] [**18**] was prepared for comparison only and was not used in reactivity studies).

The calculated force constants are not significantly different for Mo and W complexes bearing an identical set of ligands and isocyanide ligands. The substitution of two CO ligands in the {$M(CO)_5$} complex fragment for dppe leads to force constants for the C≡NR bond that are significantly smaller than the ones calculated for the pentacarbonyl complexes. This trend is particularly visible for the complexes bearing the aromatic isocyanide ligands. The substitution of two carbonyl ligands for a dppe ligand leads to a significantly enhanced electron density at the metal center and an enhanced propensity for M→C≡NR back-bonding. Stabilization of the 2-amino-functionalized aliphatic isocyanide ligands occurs if the force constant falls in a range of k < 1733 N m^{-1}. The force constant required for stabilization of the aromatic 2-aminophenyl isocyanide (k < 1668 N m^{-1}) is even smaller. These are limiting values, and not only the deactivation of the isocyanide by back-bonding (indicated by the N≡C force constant) but also the stability of the resulting ylidene influences the course of the reaction.[13a]

3. CONCLUSIONS

We presented molybdenum and tungsten complexes of aliphatic 2-aminoethyl isocyanide and aromatic 2-aminophenyl isocyanide where the ubiquitous intramolecular nucleophilic attack of the amino group at the isocyanide carbon atom has been prevented by enhanced M→C≡NR back-bonding. This allowed the isolation of complexes bearing the 2-amino-functionalized isocyanides that are unknown molecules in the free state. Limiting values for the force constants k of the C≡N bond, where intramolecular nucleophilic attack is prevented, have been calculated. These values may prove useful in the prediction of the course of reactions during the template-controlled synthesis of NH,NH-NHC complexes from isocyanide complexes.

4. EXPERIMENTAL SECTION

General Procedures. ***Caution!*** *Aliphatic azides are high-energy-density materials. Vigorous heating of 2-azidoethyl isocyanide can cause an explosive decomposition, and appropriate care is advised when handling organic azides.* All manipulations were carried out under an argon atmosphere using standard Schlenk techniques. Solvents were dried and degassed by standard methods prior to use. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were measured on Bruker AVANCE I 400, Bruker AVANCE III 400, or Bruker AVANCE II 200 spectrometers. Chemical shifts (δ) are given in parts per million using the residual protonated solvent as an internal standard. Coupling constants are expressed in hertz. Mass spectra were obtained with Orbitrap LTQ XL (Thermo Scientific), MicroTof (Bruker Daltronics), Finnigan MAT95, or Bruker Reflex IV MALDI TOF spectrometers. IR spectra were recorded on a Bruker Vector 22 spectrometer. Compounds 2-azidoethyl isocyanide **1**,[14b] 2-azidophenyl isocyanide **2**,[15a] 2-nitrophenyl isocyanide **3**,[15b] $[Mo(CO)_3(py)_3]$ [**4**],[18] and $[W(CO)_4(dppe)]$[19] have been prepared as described in the literature. Alternatively to the literature procedure,[15b] isocyanide **3** can be prepared from 2-nitrophenyl formamide by using $POCl_3$ as dehydration agent. Complex $[Mo(CO)_3(dppe)(py)]$ [**4**] was generated in situ from $[Mo(CO)_3(py)_3]$ and dppe. Elemental analyses for compounds with azido or nitro groups could not be obtained due to their potentially explosive decomposition. Instead, HRMS data are given in the Experimental Section.

$[Mo(CO)_3(dppe)(CNCH_2CH_2N_3)]$ [6]. A solution of $[Mo(CO)_3(py)_3]$ (200 mg, 0.48 mmol) in dichloromethane (20 mL) was treated with dppe (191 mg, 0.48 mmol) and left to stir for 12 h at ambient temperature. Subsequently, the solvent was removed in vacuo. The residue (crude complex [**4**]) was suspended in THF (20 mL), and to this was added dropwise a solution of 2-azidoethyl isocyanide **1** (56 mg, 0.58 mmol) in dichloromethane (10 mL). The reaction mixture was heated under reflux for 3 h, followed by removal of the solvent under reduced pressure. The crude reaction product was purified by column chromatography on neutral alumina (4% H_2O) with dichloromethane/cyclohexane (2:1, v/v) as eluent to give [**6**] as a pale yellow solid. Yield: 250 mg (0.37 mmol, 77%). ^1H NMR (400 MHz, CD_2Cl_2): δ 7.66 (m, 8H, Ph-H_{ortho}), 7.38 (m, 12H, Ph-H_{meta} and Ph-H_{para}), 2.96 (tt, ^3J = 5.8 Hz, $^5J_{PH}$ = 1.5 Hz, 2H, CH_2NC), 2.72 (t, ^3J = 5.8 Hz, 2H, CH_2N_3), 2.56 (m, 4H, CH_2P). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ 221.2 (dd, $^2J_{PC(trans)}$ = 28.5 Hz, $^2J_{PC(cis)}$ = 9.5 Hz, CO_{eq}), 215.6 (t, $^2J_{PC(cis)}$ = 8.7 Hz, CO_{ax}), 167.4 (t, $^2J_{PC}$ = 8.6 Hz, C≡

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N), 137.9 (d, $^1J_{PC}$ = 29.4 Hz, Ph-C_{ipso}), 137.7 (d, $^1J_{PC}$ = 32.0 Hz, Ph-C_{ipso}), 132.2 (m, Ph-C_{ortho}), 130.0 (Ph-C_{para}), 129.7 (Ph-C_{para}), 128.8 (m, Ph-C_{meta}), 49.7 (CH_2N_3), 42.9 (CH_2NC), 27.9 (m, CH_2P). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ 55.48. HRMS (ESI, positive ions): m/z 715.03017 [[**6**] + K]$^+$ (calcd for [[**6**] + K]$^+$ 715.03415), 699.05752 [[**6**] + Na]$^+$ (calcd for [[**6**] + Na]$^+$ 699.05905), 677.07521 [[**6**] + H]$^+$ (calcd for [[**6**] + H]$^+$ 677.07635), 649.08085 [[**6**] − CO + H]$^+$ (calcd for [[**6**] − CO + H]$^+$ 649.08335). IR (KBr, cm^{-1}): $\tilde{\nu}$ 2135 (m, C≡N and N_3), 2098 (sh, N_3), 1937 (s, CO), 1858 (s, CO), 1835 (s, CO).

[Mo(CO)$_3$(dppe)(CNCH$_2$CH$_2$NH$_3$)]X [8]X. To a suspension made up from [**6**] (289 mg, 0.43 mmol), zinc powder (38 mg, 0.58 mmol), and ammonium chloride (31 mg, 0.58 mmol) in dry methanol (20 mL) were added three drops of degassed water. This mixture was heated under reflux for 24 h. Subsequent filtration yielded a pale yellow solid containing the salts [**8**]Cl and [**8**]$_2$[$ZnCl_4$], which could not be separated. Yield: 260 mg (86% for [**8**]Cl or 78% for [**8**]$_2$[$ZnCl_4$]; the actual yield lies in between these two extremes). ^1H NMR (400 MHz, [D_6]DMSO): δ 7.68 (m, 4H, Ph-H_{ortho}), 7.63 (m, 4H, Ph-H_{ortho}), 7.40 (m, 8H, Ph-H_{meta}), 7.37 (m, 4H, Ph-H_{para}), 3.34 (br s, 3H, NH_3^+), 2.98 (t, ^3J = 6.9 Hz, 2H, CH_2NC), 2.59 (m, 4H, CH_2P), 2.10 (t, ^3J = 6.9 Hz, 2H, $CH_2NH_3^+$). $^{13}C\{^1H\}$ NMR (101 MHz, [D_6]DMSO): δ 221.5 (dd, $^2J_{PC(trans)}$ = 28.3 Hz, $^2J_{PC(cis)}$ = 9.5 Hz, CO_{eq}), 215.6 (t, $^2J_{PC(cis)}$ = 8.8 Hz, CO_{ax}), 161.1 (t, $^2J_{PC}$ = 9.6 Hz, C≡N), 136.7 (d, $^1J_{PC}$ = 32.0 Hz, Ph-C_{ipso}), 136.6 (d, $^1J_{PC}$ = 29.0 Hz, Ph-C_{ipso}), 131.5 (m, Ph-C_{ortho}), 131.2 (m, Ph-C_{ortho}), 129.5 (Ph-C_{para}), 129.4 (Ph-C_{para}), 128.4 (m, Ph-C_{meta}), 44.7 (CH_2NC), 40.2 ($CH_2NH_3^+$), 26.4 (m, CH_2P). $^{31}P\{^1H\}$ NMR (162 MHz, [D_6]-DMSO): δ 54.71. HRMS (ESI, positive ions): m/z 651.08557 [**8**]$^+$ (calcd for [**8**]$^+$ 651.08585), 623.09037 [[**8**] − CO]$^+$ (calcd for [[**8**] − CO]$^+$ 623.09286), 595.09541 [[**8**] − 2CO]$^+$ (calcd for [[**8**] − CO]$^+$ 595.09795). HRMS (ESI, negative ions): m/z 818.92543 [[**8**] − H + $ZnCl_3$]$^-$ (calcd for [[**8**] − H + $ZnCl_3$]$^-$ 818.91427), 685.05786 [[**8**] − H + Cl]$^-$ (calcd for [[**8**] − H + Cl]$^-$ 685.04752). IR (KBr, cm^{-1}): $\tilde{\nu}$ 3134 (m, NH_3^+), 2123 (m, C≡N), 1933 (s, CO), 1845 (s, CO).

[Mo(CO)$_3$(dppe)(CNCH$_2$CH$_2$NH$_2$)] [10]. A methanol solution of [**8**]X from the previous reaction was treated with an excess of sodium hydroxide. After stirring for 1 h at room temperature, the solvent was removed in vacuo. The solid residue was dissolved in a water/dichloromethane mixture. The organic layer was separated, washed several times with water, and dried over $MgSO_4$. Removal of the solvent yielded [**10**] as a pale yellow powder. Yield: 230 mg (0.35 mmol, 81%, relative to [**6**]). ^1H NMR (400 MHz, CD_2Cl_2): δ 7.67 (m, 8H, Ph-H_{ortho}), 7.36 (m, 8H, Ph-H_{meta}), 7.34 (m, 4H, Ph-H_{para}), 2.83 (t, ^3J = 5.7 Hz, 2H, CH_2NC), 2.55 (m, 4H, CH_2P), 2.18 (t, ^3J = 5.7 Hz, 2H, CH_2NH_2), 0.45 (br s, 2H, NH_2). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ 221.4 (dd, $^2J_{PC(trans)}$ = 28.5 Hz, $^2J_{PC(cis)}$ = 9.7 Hz, CO_{eq}), 216.0 (t, $^2J_{PC(cis)}$ = 8.8 Hz, CO_{ax}), 164.0 (C≡N), 137.9 (d, $^1J_{PC}$ = 27.1 Hz, Ph-C_{ipso}), 137.6 (d, $^1J_{PC}$ = 30.1 Hz, Ph-C_{ipso}), 132.1 (m, Ph-C_{ortho}), 129.9 (Ph-C_{para}), 129.7 (Ph-C_{para}), 128.8 (m, Ph-C_{meta}), 47.6 (CH_2NC), 41.4 (CH_2NH_2), 27.9 (m, CH_2P). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ 55.34. HRMS (ESI, positive ions): m/z 651.08459 [[**10**] + H]$^+$ (calcd for [[**10**] + H]$^+$ 651.08585), 623.08979 [[**10**] −CO + H]$^+$ (calcd for [[**10**] − CO + H]$^+$ 623.09286), 595.09484 [M − 2CO + H]$^+$ (calcd for [[**10**] − 2CO + H]$^+$ 595.09795). IR (KBr, cm^{-1}): $\tilde{\nu}$ 3441 (w, NH_2), 3396 (w, NH_2), 2133 (m, C≡N), 1927 (s, CO), 1831 (s, CO). Anal. Calcd: C, 59.27; H, 4.66; N, 4.32. Found: C, 59.66; H, 4.70; N, 4.00.

[W(CO)$_3$(dppe)(NCCH$_3$)] [5]. A suspension of 1.160 g (1.67 mmol) [W(CO)$_4$(dppe)][19] in acetonitrile (100 mL) was irradiated at 0 °C for 5 h in a photoreactor (high-pressure mercury vapor lamp). After complete conversion, checked by IR spectroscopy, the solvent was removed in vacuo, the oily residue was dissolved in THF and filtered through Celite. The filtrate was cooled to 0 °C and treated with hexane while stirring. Complex [**5**] precipitated out of the solvent mixture. The bright yellow solid residue was isolated by filtration and dried in vacuo. Yield: 896 mg (1.27 mmol, 76%). ^1H NMR (400 MHz, [D_8]THF): δ 7.78 (m, 4H, Ph-H_{ortho}), 7.60 (m, 4H, Ph-H_{ortho}), 7.30 (m, 12H, Ph-H_{meta} and Ph-H_{para}), 2.59 (m, 4H, CH_2-P), 1.37 (s, 3H, $NCCH_3$). $^{13}C\{^1H\}$ NMR (101 MHz, [D_8]THF): δ 215.5 (dd, $^2J_{PC(trans)}$ = 35.4 Hz, $^2J_{PC(cis)}$ = 8.4 Hz, CO_{eq}), 210.7 (t, $^2J_{PC(cis)}$ = 4.9 Hz, CO_{ax}), 137.6 (d, $^1J_{PC}$ = 40.4 Hz, Ph-C_{ipso}), 136.6 (d, $^1J_{PC}$ = 30.2 Hz, Ph-C_{ipso}), 133.7 (m, Ph-C_{ortho}), 132.9 (m, Ph-C_{ortho}), 130.2 (Ph-C_{para}), 129.7 (Ph-C_{para}), 129.2 (m, Ph-C_{meta}), 129.0 (m, Ph-C_{meta}), 123.1 (s br, $NCCH_3$), 29.5 (m, CH_2-P), 1.8 ($NCCH_3$). $^{31}P\{^1H\}$ NMR (162 MHz, [D_8]THF): δ 46.50 ($^1J_{PW}$ = 228.0 Hz). MS (MALDI, positive ions) m/z: 707 [**5**]$^+$ (calcd for [M]$^+$ 707). IR (KBr, cm^{-1}): $\tilde{\nu}$ 1918 (s, CO), 1825 (s, CO), 1793 (s, CO).

[W(CO)$_3$(dppe)(CNCH$_2$CH$_2$N$_3$)] [7]. A solution of [**5**] (225 mg, 0.32 mmol) in THF (20 mL) was treated with **1** (38.2 mg, 0.40 mmol). The reaction mixture was heated under reflux for 3 h, followed by the removal of the solvent under reduced pressure. The crude reaction product was purified by column chromatography on neutral alumina (4% H_2O) with dichloromethane/cyclohexane (2:1, v/v) as eluent to give [**7**] as a pale yellow solid. Yield: 172 mg (0.23 mmol, 72%). ^1H NMR (400 MHz, CD_2Cl_2): δ 7.65 (m, 8H, Ph-H_{ortho}), 7.38 (m, 8H, Ph-H_{meta}), 7.35 (m, 4H, Ph-H_{para}), 2.98 (tt, ^3J = 5.9 Hz, $^5J_{PH}$ = 1.5 Hz, 2H, CH_2NC), 2.69 (t, ^3J = 5.9 Hz, 2H, CH_2N_3), 2.61 (m, 4H, CH_2P). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ 212.6 (dd, $^2J_{PC(trans)}$ = 27.8 Hz, $^2J_{PC(cis)}$ = 7.5 Hz, CO_{eq}), 207.0 (t, $^2J_{PC(cis)}$ = 6.4 Hz, CO_{ax}), 159.5 (C≡N), 137.4 (d, $^1J_{PC}$ = 35.4 Hz, Ph-C_{ipso}), 137.2 (d, $^1J_{PC}$ = 38.1 Hz, Ph-C_{ipso}), 132.3 (m, Ph-C_{ortho}), 130.1 (Ph-C_{para}), 129.9 (Ph-C_{para}), 128.9 (m, Ph-C_{meta}), 49.8 (CH_2N_3), 43.0 (CH_2NC), 29.5 (m, CH_2P). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ 40.71 ($^1J_{PW}$ = 222.7 Hz). MS (EI): m/z (%) 762 (20) [**7**]$^+$, 734 (54) [[**7**] − CO]$^+$, 706 (86) [[**7**] − 2CO]$^+$, 678 (56) [[**7**] − 3CO]. HRMS (ESI, positive ions): m/z 762.11465 [**7**]$^+$ (calcd for [**7**]$^+$ 762.11465). IR (KBr, cm^{-1}): $\tilde{\nu}$ 2129 (m, C≡N and N_3), 2097 (m, N_3), 1934 (s, CO), 1852 (s, CO), 1821 (s, CO).

[W(CO)$_3$(dppe)(CNCH$_2$CH$_2$NH$_3$)]X [9]X. To a suspension of [**7**] (102 mg, 0.13 mmol), zinc powder (18 mg, 0.27 mmol), and NH_4Cl (15 mg, 0.28 mmol) in methanol (20 mL) was added 0.1 mL of degassed water. The reaction mixture was heated under reflux for 24 h. After removal of the solvent, the residue was dissolved in dichloromethane and filtered. Removal of the solvent yielded a pale yellow powder. The obtained solid is composed of the salts [**9**]Cl and [**9**]$_2$[$ZnCl_4$], which could not be separated. Yield: 106 mg. ^1H NMR (400 MHz, CD_2Cl_2): δ 7.64 (m, 8H, Ph-H_{ortho}), 7.44 (m, 4H, Ph-H_{para}), 7.37 (m, 8H, Ph-H_{meta}), 3.12 (t, ^3J = 5.6 Hz, 2H, CH_2NC), 2.63 (m, 4H, CH_2P), 2.46 (t, ^3J = 5.6 Hz, 2H, CH_2NH_3), 2.23 (s br, 3H, NH_3). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ 212.9 (dd, $^2J_{PC(trans)}$ = 27.7 Hz, $^2J_{PC(cis)}$ = 7.7 Hz, CO_{eq}), 207.2 (t, $^2J_{PC(cis)}$ = 6.6 Hz, CO_{ax}), 159.2 (C≡N), 137.4 (d, $^1J_{PC}$ = 35.1 Hz, Ph-C_{ipso}), 137.1 (d, $^1J_{PC}$ = 37.7 Hz, Ph-C_{ipso}), 132.4 (m, Ph-C_{ortho}), 132.1 (m, Ph-C_{ortho}), 130.2 (Ph-C_{para}), 130.2 (Ph-C_{para}), 129.2 (m, Ph-C_{meta}), 128.9 (m, Ph-C_{meta}), 45.4 (CH_2NC), 41.1 (CH_2NH_3), 29.6 (m, CH_2P). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ 40.80 ($^1J_{PW}$ = 222.1 Hz). HRMS (ESI, positive ions): m/z 737.13228 [**9**]$^+$ (calcd for [**9**]$^+$ 737.13190). HRMS (ESI, negative ions): m/z 771.0997 [[**9**] − H + Cl]$^-$ (calcd for [[**9**] − H + Cl]$^-$ 771.0886). IR (KBr, cm^{-1}): $\tilde{\nu}$ 3193 (w, NH_3^+), 2125 (m, C≡N), 1929 (s, CO), 1849 (s, CO).

[W(CO)$_3$(dppe)(CNCH$_2$CH$_2$NH$_2$)] [11]. A solution of [**9**]X from the previous reaction in 10 mL of methanol was treated with sodium hydroxide and stirred for 1 h at room temperature. After removal of the solvent, the residue was dissolved in water and dichloromethane. The organic layer was separated, washed several times with water, and dried over $MgSO_4$. Removal of the solvent yielded [**11**] as a pale yellow powder. Yield: 58 mg (0.08 mmol, 62%, relative to [**7**]). ^1H NMR (200 MHz, CD_2Cl_2): δ 7.65 (m, 8H, Ph-H_{ortho}), 7.39 (m, 12H, Ph-H_{meta} and Ph-H_{para}), 2.85 (tt, ^3J = 5.8 Hz, $^5J_{PC}$ = 1.5 Hz, 2H, CH_2NC), 2.61 (m, 4H, CH_2P), 2.16 (t, ^3J = 5.8 Hz, 2H, CH_2NH_2), 0.61 (s br, 2H, NH_2). $^{13}C\{^1H\}$ NMR (50 MHz, CD_2Cl_2): δ 212.9 (dd, $^2J_{PC(trans)}$ = 27.9 Hz, $^2J_{PC(cis)}$ = 7.7 Hz, CO_{eq}), 207.4 (t, $^2J_{PC(cis)}$ = 6.5 Hz, CO_{ax}), 156.0 (C≡N), 137.5 (d, $^1J_{PC}$ = 34.6 Hz, Ph-C_{ipso}), 137.2 (dd, $^1J_{PC}$ = 38.1 Hz, $^3J_{PC}$ = 0.9 Hz, Ph-C_{ipso}), 132.2 (m, Ph-C_{ortho}), 130.1 (Ph-C_{para}), 129.9 (Ph-C_{para}), 128.9 (m, Ph-C_{meta}), 47.7 (CH_2NC), 41.5 (CH_2NH_2), 29.5 (m, CH_2P). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ 40.63 ($^1J_{PW}$ = 222.6 Hz). MS (EI): m/z (%) 736 (85) [**11**]$^+$, 708 (100) [[**11**] − CO]$^+$, 680 (62) [[**11**] − 2CO]$^+$, 652 (30) [[**11**] − 3CO], 638 (22) [[**11**] − $CNCH_2CH_2NH_2$ − CO], 610 (18) [[**11**] −

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$CNCH_2CH_2NH_2$ − 2CO], 582 (7) [[**11**] − $CNCH_2CH_2NH_2$ − 3CO]. HRMS (ESI, positive ions): *m/z* 737.13025 [[**11**] + H]$^+$ (calcd for [[**11**] + H]$^+$ 737.13138). IR (KBr, cm^{-1}): $\tilde{\nu}$ 3447 (w, NH_2), 3363 (w, NH_2), 2126 (m, C≡N), 1926 (s, CO), 1838 (s, CO). Anal. Calcd: C, 52.19; H, 4.11; N, 3.80. Found: C, 51.10; H, 4.00; N, 3.58.

[Mo(CO)$_3$(dppe)(CNC$_6$H$_4$N$_3$)] [12]. See preparation of [**16**].

[Mo(CO)$_3$(dppe)(CNC$_6$H$_4$NO$_2$)] [13]. A solution of [Mo(CO)$_3$(py)$_3$] (288 mg, 0.69 mmol) dissolved in dichloromethane (20 mL) was treated with 275 mg (0.69 mmol) of dppe and left to stir for 12 h at room temperature. Subsequently, the solvent was removed in vacuo. The residue (complex [**4**]) was not further purified but was suspended in THF (20 mL). To this suspension was added dropwise a solution of **3** (123 mg, 0.83 mmol) in dichloromethane (10 mL). The reaction mixture was heated under reflux for 4.5 h, followed by the removal of the solvents under reduced pressure. The crude reaction product was purified by column chromatography on neutral alumina (4% H_2O) with dichloromethane/cyclohexane (1:1, v/v) as eluent to give [**13**] as a deep red solid. Yield: 282 mg (0.39 mmol, 57%). ^{1}H NMR (400 MHz, [D$_8$]THF): δ 7.91 (dd, ^3J = 8.2 Hz, ^4J = 0.9 Hz, 1H, H-3), 7.68 (m, 8H, Ph-H$_{ortho}$), 7.40 (ddd, ^3J = 8.2 Hz, ^3J = 8.0 Hz, ^4J = 0.9 Hz, H-5), 7.34 (m, 4H, Ph-H$_{meta}$), 7.30 (m, 2H, Ph-H$_{para}$), 7.26 (ddd, ^3J = 8.2 Hz, ^3J = 8.1 Hz, ^4J = 0.9 Hz, 1H, H-4), 7.19 (m, 4H, Ph-H$_{meta}$), 7.12 (m, 2H, Ph-H$_{para}$), 6.55 (dd, ^3J = 7.9 Hz, ^4J = 0.9 Hz, 1H, H-6), 2.64 (m, 4H, CH_2P). ^{13}C{^{1}H} NMR (101 MHz, [D$_8$]THF): δ 220.3 (dd, $^2J_{PC(trans)}$ = 27.7 Hz, $^2J_{PC(cis)}$ = 9.1 Hz, CO$_{eq}$), 214.9 (t, $^2J_{PC(cis)}$ = 8.8 Hz, CO$_{ax}$), 188.0 (t, $^2J_{PC}$ = 10.3 Hz, C≡N), 143.2 (C-2), 138.5 (d, $^1J_{PC}$ = 32.2 Hz, Ph-C$_{ipso}$), 138.4 (d, $^1J_{PC}$ = 31.4 Hz, Ph-C$_{ipso}$), 134.7 (C-5), 132.7 (m, Ph-C$_{ortho}$), 130.7 (C-6), 130.3 (Ph-C$_{para}$), 129.8 (Ph-C$_{para}$), 129.1 (m, Ph-C$_{meta}$), 127.6 (C-4), 126.0 (C-3), 123.5 (C-1), 28.6 (m, CH_2P). ^{31}P{^{1}H} NMR (162 MHz, [D$_8$]THF): δ 56.45. HRMS (ESI, positive ions): *m/z* 751.04371 [[**13**] + Na]$^+$ (calcd for [[**13**] + Na]$^+$ 751.04283). HRMS (ESI, negative ions): *m/z* 763.02591 [[**13**] + Cl]$^-$ (calcd for [[**13**] + Cl]$^-$ 763.02128). IR (KBr, cm^{-1}): $\tilde{\nu}$ 2063 (m, C≡N), 1925 (s, CO), 1876 (s, CO).

[W(CO)$_3$(dppe)(CNC$_6$H$_4$N$_3$)] [14]. See preparation of [**17**].

[W(CO)$_3$(dppe)(CNC$_6$H$_4$NO$_2$)] [15]. A solution of [**5**] (239 mg, 0.34 mmol) dissolved in THF (40 mL) was treated dropwise with a solution of **3** (50 mg, 0.34 mmol) in THF (20 mL). The reaction mixture was stirred for 20 h at ambient temperature, and the solvent was subsequently removed under reduced pressure. The obtained solid was purified by column chromatography on neutral alumina (4% H_2O) with dichloromethane as eluent to give [**15**] as a red solid. Yield: 246 mg (0.30 mmol, 88%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.89 (dd, ^3J = 8.3 Hz, ^4J = 1.4 Hz, 1H, H-3), 7.64 (m, 8H, Ph-H$_{ortho}$), 7.38 (m, 4H, Ph-H$_{meta}$), 7.37 (m, 2H, Ph-H$_{para}$), 7.34 (m, 1H, H-5), 7.23 (m, 1H, H-4), 7.23 (m, 4H, Ph-H$_{meta}$), 7.16 (m, 2H, Ph-H$_{para}$), 6.50 (dd, ^3J = 8.0 Hz, ^4J = 1.3 Hz, H-6), 2.69 (m, 4H, CH_2P). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2): δ 211.4 (dd, $^2J_{PC(trans)}$ = 26.9 Hz, $^2J_{PC(cis)}$ = 7.5 Hz, CO$_{eq}$), 206.8 (t, $^2J_{PC(cis)}$ = 6.7 Hz, CO$_{ax}$), 179.0 (C≡N), 142.5 (C-2), 137.0 (d, $^1J_{PC}$ = 38.8 Hz, Ph-C$_{ipso}$), 136.9 (d, $^1J_{PC}$ = 37.4 Hz, Ph-C$_{ipso}$), 134.3 (C-5), 132.2 (m, Ph-C$_{ortho}$), 130.3 (Ph-C$_{para}$), 130.2 (C-6), 129.8 (Ph-C$_{para}$), 128.9 (m, Ph-C$_{meta}$), 126.9 (C-4), 125.6 (C-3), 123.6 (C-1), 29.8 (m, CH_2P). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ 40.60 ($^1J_{PW}$ = 225.3 Hz). HRMS (ESI, positive ions): *m/z* 837.0843 [[**15**] + Na]$^+$ (calcd for [[15] + Na]$^+$ 837.0881), 815.1061 [[**15**] + H]$^+$ (calcd for [[**15**] + H]$^+$ 815.1061). MS (MALDI, positive ions): *m/z*: 814 [**15**]$^+$, 730 [[**15**] − 3CO]$^+$. IR (KBr, cm^{-1}): $\tilde{\nu}$ 2059 (m, C≡N), 1919 (s, CO), 1857 (s, CO).

[Mo(CO)$_3$(dppe)(CNC$_6$H$_4$NH$_2$)] [16] by Reduction of the Azidophenyl Isocyanide in [12]. Complex [**12**] was prepared as described below and used without further purification for the subsequent reduction. A solution of [Mo(CO)$_3$(py)$_3$] (129 mg, 0.31 mmol) in dichloromethane (20 mL) was treated with dppe (123 mg, 0.31 mmol) and left to stir for 12 h at ambient temperature. Subsequently, the solvent was removed in vacuo. The solid residue (complex [**4**]) was suspended in THF (20 mL), and to this solution was added dropwise 2-azidophenyl isocyanide **2** (53 mg, 0.37 mmol) dissolved in THF (20 mL). The reaction mixture was heated under reflux for 12 h, followed by the removal of the solvent under reduced pressure. The oily residue of [**12**] obtained this way proved difficult to purify without decomposition and was, therefore, used as received for the next reaction. Complex [**12**] was characterized by IR spectroscopy (KBr, cm^{-1}): $\tilde{\nu}$ 2121 (m, N_3), 2077 (m, C≡N), 1929 (s, CO), 1856 (s, CO). The oily residue of [**12**] was dissolved in THF (20 mL), and zinc powder (27 mg, 0.42 mmol), ammonium chloride (23 mg, 0.43 mmol), and three drops of degassed water were added. The resulting suspension was heated under reflux for 24 h. The solvent was then removed in vacuo. The residue was dissolved in methanol (10 mL) and treated with sodium hydroxide (22 mg, 0.55 mmol). The reaction mixture was stirred at ambient temperature for 1 h. After removal of the solvent, dichloromethane (20 mL) and water (10 mL) were added. The organic layer was separated, washed several times with water, and dried over $MgSO_4$. Removal of the solvent gave a solid residue that was purified by column chromatography on silica gel with dichloromethane/cyclohexane (1:1, v/v) as eluent to give [**16**] as a slightly yellow powder. Yield: 184 mg (0.26 mmol, 84% over the entire reaction sequence starting from [Mo(CO)$_3$(py)$_3$]). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.68 (m, 8H, Ph-H$_{ortho}$), 7.38 (m, 4H, Ph-H$_{meta}$), 7.37 (m, 2H, Ph-H$_{para}$), 7.28 (m, 4H, Ph-H$_{meta}$), 7.26 (m, 2H, Ph-H$_{para}$), 6.94 (ddd, ^3J = 8.1 Hz, ^3J = 7.9 Hz, ^4J = 1.2 Hz, 1H, H-4), 6.55 (dd, ^3J = 8.1 Hz, ^4J = 0.9 Hz, 1H, H-3), 6.45 (ddd, ^3J = 7.9 Hz, ^3J = 7.8 Hz, ^4J = 0.9 Hz, 1H, H-5), 6.26 (dd, ^3J = 7.8 Hz, ^4J = 1.2 Hz, 1H, H-6), 3.40 (br s, 2H, NH_2), 2.59 (m, 4H, CH_2P). ^{1}H NMR (400 MHz, [D$_8$]THF): δ 7.71 (m, 8H, Ph-H$_{ortho}$), 7.31 (m, 6H, Ph-H$_{para}$ and Ph-H$_{meta}$), 7.25 (m, 4H, Ph-H$_{meta}$), 7.20 (m, 2H, Ph-H$_{para}$), 6.85 (ddd, ^3J = 8.2 Hz, ^3J = 7.2 Hz, ^4J = 1.2 Hz, 1H, H-4), 6.54 (dd, ^3J = 8.2 Hz, ^4J = 0.9 Hz, 1H, H-3), 6.30 (ddd, ^3J = 8.0 Hz, ^3J = 7.2 Hz, ^4J = 0.9 Hz, 1H, H-5), 6.17 (dd, ^3J = 8.0 Hz, ^4J = 1.2 Hz, 1H, H-6), 4.20 (s, 2H, NH_2), 2.60 (m, 4H, CH_2P). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2): δ 220.9 (dd, $^2J_{PC(trans)}$ = 28.4 Hz, $^2J_{PC(cis)}$ = 9.6 Hz, CO$_{eq}$), 215.9 (t, $^2J_{PC(cis)}$ = 8.6 Hz, CO$_{ax}$), 176.4 (t, $^2J_{PC}$ = 10.0 Hz, C≡N), 142.9 (C-2), 138.0 (d, $^1J_{PC}$ = 29.8 Hz, Ph-C$_{ipso}$), 137.5 (d, $^1J_{PC}$ = 32.1 Hz, Ph-C$_{ipso}$), 132.3 (m, Ph-C$_{ortho}$), 131.9 (m, Ph-C$_{ortho}$), 130.1 (Ph-C$_{para}$), 129.7 (Ph-C$_{para}$), 128.9 (m, Ph-C$_{meta}$), 128.9 (C-4), 126.2 (C-6), 117.9 (C-5), 115.3 (C-3), 115.1 (C-1), 27.9 (m, CH_2P). ^{13}C{^{1}H} NMR (101 MHz, [D$_8$]THF): δ 221.1 (dd, $^2J_{PC(trans)}$ = 28.3 Hz, $^2J_{PC(cis)}$ = 9.4 Hz, CO$_{eq}$), 216.0 (t, $^2J_{PC(cis)}$ = 8.7 Hz, CO$_{ax}$), 177.1 (C≡N), 144.7 (C-2), 139.0 (d, $^1J_{PC}$ = 29.6 Hz, Ph−C$_{ipso}$), 138.5 (d, $^1J_{PC}$ = 31.7 Hz, Ph-C$_{ipso}$), 132.9 (m, Ph-C$_{ortho}$), 132.5 (m, Ph-C$_{ortho}$), 130.2 (Ph-C$_{para}$), 129.9 (Ph-C$_{para}$), 129.1 (m, Ph-C$_{meta}$), 129.1 (C-4), 126.5 (C-6), 116.9 (C-5), 115.3 (C-3), 115.2 (C-1), 28.4 (m, CH_2P). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ 55.10. ^{31}P{^{1}H} NMR (162 MHz, [D$_8$]THF): δ 55.82. MS (EI): *m/z* (%) 698 (5) [**16**]$^+$, 670 (13) [[**16**] − CO]$^+$, 642 (9) [[**16**] − 2CO]$^+$, 614 (5) [[**16**] − 3CO]$^+$, 580 (17) [[**16**] − $CNC_6H_4NH_2$]$^+$, 552 (25) [[**16**] − CO − $CNC_6H_4NH_2$]$^+$, 524 (30) [[**16**] − 2CO −$CNC_6H_4NH_2$]$^+$, 496 (50) [[**16**] − 3CO − $CNC_6H_4NH_2$]$^+$. HRMS (ESI, positive ions): *m/z* 721.06882 [[**16**] + Na]$^+$ (calcd for [[**16**] + Na]$^+$ 721.06863). HRMS (ESI, negative ions): *m/z* 733.05107 [[**16**] + Cl]$^-$ (calcd for [[**16**] + Cl]$^-$ 733.05107). IR (KBr, cm^{-1}): $\tilde{\nu}$ 3484 (m, NH_2), 3394 (m, NH_2), 2097 (m, NC), 1924 (s, CO), 1848 (s, CO), 1822 (s, CO). Anal. Calcd: C, 62.08; H, 4.34; N, 4.02. Found: C, 61.76; H, 4.54; N, 3.76.

[Mo(CO)$_3$(dppe)(CNC$_6$H$_4$NH$_2$)] [16] by Reduction of the Nitrophenyl Isocyanide in [13]. A solution of [**13**] (212 mg, 0.29 mmol) in THF (20 mL) was treated with a catalytic amount of Raney nickel. The mixture was cooled to 0 °C and treated dropwise with hydrazine hydrate (0.3 mL, 5.80 mmol). After warm-up, the reaction mixture was stirred for 48 h at ambient temperature. Removal of insolubles by filtration and stripping of the solvent gave an off-white powder that was purified by column chromatography on silica gel with dichloromethane/cyclohexane (1:1, v/v) as eluent to give [**16**] as a slightly yellow powder. Yield: 141 mg (0.20 mmol, 69%). The analytical data are identical to those of [**16**] obtained from [**12**].

[W(CO)$_3$(dppe)(CNC$_6$H$_4$NH$_2$)] [17] by Reduction of the Azidophenyl Isocyanide in [14]. A sample of complex [**5**] (180 mg, 0.25 mmol) dissolved in THF (20 mL) was treated with a solution of **2** (44 mg, 0.30 mmol) in THF (5 mL). The reaction mixture was heated under reflux for 12 h. Removal of the solvent gave complex [**14**] as an oily residue that proved difficult to purify without decomposition. The complex was, therefore, used as received for the

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subsequent reduction. Crude complex [**14**] was characterized by IR spectroscopy (KBr, cm^{-1}): $\tilde{\nu}$ 2123 (m, N_3), 2075 (m, C≡N), 1921 (s, CO), 1851 (s, CO). The crude complex [**14**] was dissolved in THF (20 mL), and zinc powder (23 mg, 0.35 mmol), ammonium chloride (19 mg, 0.35 mmol), and three drops of degassed water were added. The suspension was heated for 24 h under reflux. Subsequently, the solvent was removed in vacuo and the solid residue was dissolved in methanol (10 mL) and treated with sodium hydroxide (22 mg, 55 mmol) dissolved in methanol (10 mL). The reaction mixture was stirred for 1 h at ambient temperature, followed by removal of the solvent in vacuo at ambient temperature. Dichloromethane (20 mL) and water (10 mL) were added. The organic layer was separated, washed several times with water, and dried over $MgSO_4$. Removal of the solvent gave a yellow powder. This powder was purified by column chromatography on silica gel with dichloromethane/cyclohexane (3:1, v/v) as eluent to give [**17**] as a slightly yellow powder. Yield: 60 mg (0.08 mmol, 31%). For analytical data, see below.

[W(CO)$_3$(dppe)(CNC$_6$H$_4$NH$_2$)] [17] by Reduction of the Nitrophenyl Isocyanide in [15]. A solution of [**15**] (176 mg, 0.22 mmol) in THF (20 mL) was treated with a catalytic amount of Raney nickel. The mixture was cooled to 0 °C and treated dropwise with hydrazine hydrate (0.3 mL, 5.80 mmol). After warm-up, the reaction mixture was stirred for 72 h at ambient temperature. Removal of insolubles by filtration and stripping of the solvent gave an off-white powder that was purified by column chromatography on silica gel with dichloromethane/cyclohexane (1:1, v/v) as eluent to give [**17**] as a slightly yellow powder. Yield: 78 mg (0.10 mmol, 45%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.65 (m, 8H, Ph-H$_{ortho}$), 7.39 (m, 6H, Ph-H$_{para}$ and Ph-H$_{meta}$), 7.29 (m, 4H, Ph-H$_{meta}$), 7.27 (m, 2H, Ph-H$_{para}$), 6.93 (ddd, ^3J = 7.9 Hz, ^3J = 7.7 Hz, ^4J = 1.2 Hz, 1H, H-4), 6.54 (dd, ^3J = 7.9 Hz, ^4J = 0.8 Hz, 1H, H-3), 6.44 (ddd, ^3J = 7.9 Hz, ^3J = 7.7 Hz, ^4J = 0.8 Hz, 1H, H-5), 6.21 (dd, ^3J = 7.9 Hz, ^4J = 1.2 Hz, 1H, H-6), 3.39 (s, 2H, NH_2), 2.65 (m, 4H, CH_2P). ^{1}H NMR (400 MHz, [D_8]THF): δ 7.70 (m, 8H, Ph-H$_{ortho}$), 7.32 (m, 6H, Ph-H$_{para}$ and Ph-H$_{meta}$), 7.26 (m, 4H, Ph-H$_{meta}$), 7.19 (m, 2H, Ph-H$_{para}$), 6.83 (ddd, ^3J = 8.2 Hz, ^3J = 7.3 Hz, ^4J = 1.5 Hz, 1H, H-4), 6.52 (dd, ^3J = 8.2 Hz, ^4J = 1.2 Hz, 1H, H-3), 6.29 (ddd, ^3J = 7.9 Hz, ^3J = 7.3 Hz, ^4J = 1.2 Hz, 1H, H-5), 6.12 (dd, ^3J = 7.9 Hz, ^4J = 1.5 Hz, 1H, H-6), 4.19 (s, 2H, NH_2), 2.67 (m, 4H, CH_2P). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2): δ 212.3 (dd, $^2J_{PC(trans)}$ = 27.5 Hz, $^2J_{PC(cis)}$ = 7.2 Hz, CO$_{eq}$), 207.7 (t, $^2J_{PC(cis)}$ = 6.5 Hz, CO$_{ax}$), 168.9 (t, $^2J_{PC)}$ = 8.2 Hz, C≡N), 143.0 (C-2), 137.5 (d, $^1J_{PC}$ = 36.2 Hz, Ph-C$_{ipso}$), 137.0 (d, $^1J_{PC}$ = 38.2 Hz, Ph-C$_{ipso}$), 132.4 (m, Ph-C$_{ortho}$), 131.9 (m, Ph-C$_{ortho}$), 130.3 (Ph-C$_{para}$), 129.9 (Ph-C$_{para}$), 129.0 (m, Ph-C$_{meta}$), 128.7 (C-4), 126.2 (C-6), 117.9 (C-5), 115.4 (C-1), 115.3 (C-3), 29.5 (m, CH_2P). ^{13}C{^{1}H} NMR (101 MHz, [D_8]THF): δ 212.3 (dd, $^2J_{PC(trans)}$ = 27.7 Hz, $^2J_{PC(cis)}$ = 7.5 Hz, CO$_{eq}$), 207.7 (t, $^2J_{PC(cis)}$ = 6.3 Hz, CO$_{ax}$), 169.3 (t, $^2J_{PC}$ = 7.8 Hz, C≡N), 144.8 (C-2), 138.5 (d, $^1J_{PC}$ = 35.7 Hz, Ph-C$_{ipso}$), 138.1 (d, $^1J_{PC}$ = 38.3 Hz, Ph-C$_{ipso}$), 133.0 (m, Ph-C$_{ortho}$), 132.5 (m, Ph-C$_{ortho}$), 130.4 (Ph-C$_{para}$), 130.1 (Ph-C$_{para}$), 129.2 (m, Ph-C$_{meta}$), 129.1 (m, Ph-C$_{meta}$), 128.8 (C-4), 126.4 (C-6), 116.9 (C-5), 115.5 (C-1), 115.3 (C-3), 30.0 (m, CH_2P). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ 40.25 ($^1J_{PW}$ = 223.7 Hz). ^{31}P{^{1}H} NMR (162 MHz, [D_8]THF): δ 40.95 ($^1J_{PW}$ = 225.3 Hz). HRMS (ESI, positive Ions): m/z 807.11346 [[**17**] + Na]$^+$ (calcd for [[**17**] + Na]$^+$ 807.11391), 785.13149 [[**17**] + H]$^+$ (calcd for [[**17**] + H]$^+$ 785.13197). HRMS (ESI, negative Ions): m/z 819.10153 [[**17**] + Cl]$^-$ (calcd for [[**17**] + Cl]$^-$ 819.09187). MS (MALDI, positive ions): m/z 784 [**17**]$^+$. IR (KBr, cm^{-1}): $\tilde{\nu}$ 3482 (w, NH_2), 3389 (w, NH_2), 2093 (m, C≡N), 1917 (s, CO), 1841 (s, CO), 1817 (s, CO). Anal. Calcd: C, 55.12; H, 3.85; N, 3.57. Found: C, 55.06; H, 3.93; N, 3.31.

[Mo(CO)$_5$(CNCH$_2$CH$_2$N$_3$)] [18]. A solution of [Mo(CO)$_6$] (200 mg, 0.76 mmol) and 2-azidoethyl isocyanide **1** (73 mg, 0.76 mmol) in THF (15 mL) was treated dropwise with a solution of trimethylamine oxide (84 mg, 1.12 mmol) in dichloromethane (30 mL). The reaction mixture was stirred at ambient temperature for 6 h. After removal of the solvent, the residue was extracted with diethyl ether. Stripping of the solvent gave a purple powder that was purified by column chromatography on neutral alumina with dichloromethane/cyclohexane (1:1, v/v) as eluent to give [**18**] as a pink to purple solid. Yield: 56 mg (0.17 mmol, 22%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.78 (t, ^3J = 5.6 Hz, 2H, CH_2N_3), 3.60 (t, ^3J = 5.6 Hz, 2H, CH_2NC). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 206.4 (CO$_{ax}$), 203.6 (CO$_{eq}$), 157.3 (C≡N), 49.5 (CH_2N_3), 43.7 (CH_2NC). MS (EI): m/z (%) 334 (100) [**18**]$^+$ 306 (27) [[**18**] − CO]$^+$, 278 (11) [[**18**] − 2CO]$^+$, 250 (49) [[**18**] − 3CO]$^+$, 222 (75) [[**18**] − 4CO]$^+$, 194 (44) [[**18**] − 5CO]$^+$. IR (KBr, cm^{-1}): $\tilde{\nu}$ 2176 (s, C≡N), 2132 (sh, N_3), 2106 (s, N_3), 2072 (s, CO), 1929 (s, CO).

X-ray Diffraction Studies. Diffraction data were collected at T = 153(2) K with a Bruker AXS APEX CCD diffractometer ([**6**], [**6**]$_2$·2CH_2Cl_2, [**10**], [**13**]·THF, and [**15**]·Et_2O) or a STOE IPDS 2 ([**16**] and [**17**]) diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Diffraction data were collected over the full sphere and were corrected for absorption. Structure solutions were found with the SHELXS-97[26] package using direct methods and were refined with SHELXL-97[26] against $|F^2|$ using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure models in calculated positions.

[**6**]. Crystals suitable for a X-ray diffraction study were obtained by slow evaporation of the solvent from a THF solution of [**6**]. $C_{32}H_{28}N_4MoO_3P_2$, M = 674.46 g·mol^{-1}, light yellow crystal, 0.07 × 0.06 × 0.05 mm^3, orthorhombic, space group $Pna2_1$, Z = 4, a = 22.5033(8) Å, b = 9.8583(4) Å, c = 13.5324(5) Å, V = 3002.1(2) Å^3, ρ_{calc} = 1.492 g·cm^{-3}, μ = 0.584 mm^{-1}, ω- and φ-scans, 34 439 measured intensities ($3.6° \le 2\theta \le 60.5°$), semiempirical absorption correction ($0.960 \le T \le 0.971$), 8868 independent (R_{int} = 0.0285) and 8207 observed intensities ($I \ge 2\sigma(I)$), refinement of 379 parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions. R = 0.0224, wR = 0.0481, R_{all} = 0.0266, wR_{all} = 0.0499. The asymmetric unit contains one formula unit.

[**6**]$_2$·2CH_2Cl_2. Crystals of [**6**]$_2$·2CH_2Cl_2 suitable for an X-ray diffraction study were obtained by slow evaporation of the solvent from a dichloromethane solution of [**6**]$_2$. $C_{66}H_{60}N_8Cl_4Mo_2O_6P_4$, M = 1518.78 g·mol^{-1}, colorless stick, 0.07 × 0.03 × 0.03 mm^3, monoclinic, space group $P2_1/n$, Z = 2, a = 18.5649(7) Å, b = 9.7263(3) Å, c = 19.0379(7) Å, β = 97.8670(10)°, V = 3405.3(2) Å^3, ρ_{calc} = 1.481 g·cm^{-3}, μ = 0.675 mm^{-1}, ω- and φ-scans, 35 449 measured intensities ($2.9° \le 2\theta \le 59.5°$), semiempirical absorption correction ($0.954 \le T \le 0.980$), 9606 independent (R_{int} = 0.0506) and 7352 observed intensities ($I \ge 2\sigma(I)$), refinement of 406 parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions. R = 0.0395, wR = 0.0894, R_{all} = 0.0610, wR_{all} = 0.0988. The asymmetric unit contains one-half a formula unit related to the other half by a crystallographic inversion center.

[**10**]. Crystals suitable for an X-ray diffraction study were obtained by slow diffusion of diethyl ether into a saturated solution of [**10**] in dichloromethane. $C_{32}H_{30}N_2MoO_3P_2$, M = 648.46 g·mol^{-1}, light yellow crystal, 0.10 × 0.07 × 0.03 mm^3, monoclinic, space group Cc, Z = 4, a = 22.1752(10) Å, b = 8.6798(4) Å, c = 15.6483(7) Å, β = 104.3190(10)°, V = 2918.4(2) Å^3, ρ_{calc} = 1.476 g·cm^{-3}, μ = 0.595 mm^{-1}, ω- and φ-scans, 16 832 measured intensities ($3.8° \le 2\theta \le 60.6°$), semiempirical absorption correction ($0.943 \le T \le 0.982$), 8406 independent (R_{int} = 0.0192) and 8036 observed intensities ($I \ge 2\sigma(I)$), refinement of 389 parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions. R = 0.0220, wR = 0.0523, R_{all} = 0.0239, wR_{all} = 0.0530. The asymmetric unit contains one formula unit.

[**13**]·THF. Crystals of [**13**]·THF suitable for an X-ray diffraction study were obtained by slow evaporation of the solvent from a THF solution of [**13**]. $C_{40}H_{36}N_2MoO_6P_2$, M = 798.59 g·mol^{-1}, dark red crystal, 0.13 × 0.09 × 0.08 mm^3, triclinic, space group $P\bar{1}$, Z = 2, a = 11.9644(5) Å, b = 12.2905(5) Å, c = 13.6395(6) Å, α = 98.6020(10)°, β = 105.1870(10)°, γ = 103.3640(10)°, V = 1835.45(13) Å^3, ρ_{calc} = 1.445 g·cm^{-3}, μ = 0.494 mm^{-1}, ω- and φ-scans, 21 265 measured intensities ($3.2° \le 2\theta \le 60.0°$), semiempirical absorption correction ($0.939 \le T \le 0.962$), 10 572 independent (R_{int} = 0.0241) and 9444 observed intensities ($I \ge 2\sigma(I)$), refinement of 460 parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions. R = 0.0313, wR = 0.1053, R_{all} = 0.0355, wR_{all} = 0.1086. The asymmetric unit contains one formula unit.

[**15**]·Et_2O. Crystals of [**15**]·Et_2O suitable for an X-ray diffraction study were obtained by slow evaporation of the solvent from a diethyl ether solution of [**15**]. $C_{40}H_{38}N_2O_6P_2W$, M = 888.51 g·mol^{-1}, brown crystal, 0.05 × 0.03 × 0.02 mm^3, triclinic; space group $P\bar{1}$, Z = 2, a = 11.9808(10) Å, b = 12.1509(10) Å, c = 13.7515(11) Å, α = 100.148(1)°, β = 100.671(1)°, γ = 103.831(1)°, V = 1858.6(3) Å^3, ρ_{calc} = 1.588 g·cm^{-3}, μ = 3.243 mm^{-1}, ω- and φ-scans, 19 135 measured intensities (3.1° ≤ 2θ ≤ 55.8°), semiempirical absorption correction (0.855 ≤ T ≤ 0.938), 8836 independent (R_{int} = 0.0298) and 7775 observed intensities ($I \geq 2\sigma(I)$), refinement of 460 parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions. R = 0.0281, wR = 0.0591, R_{all} = 0.0355, wR_{all} = 0.0615. The asymmetric unit contains one formula unit. The diethyl ether molecule in the asymmetric unit is disordered.

[**16**]. Crystals suitable for an X-ray diffraction study were obtained by slow evaporation of the solvent from a dichloromethane solution of [**16**]. $C_{36}H_{30}MoN_2O_3P_2$, M = 696.50 g·mol^{-1}, colorless crystal, 0.28 × 0.22 × 0.04 mm^3, orthorhombic, space group *Pbca*, Z = 8, a = 16.810(3) Å, b = 16.578(3) Å, c = 22.578(5) Å, V = 6292(2) Å^3, ρ_{calc} = 1.471 g·cm^{-3}, μ = 0.558 mm^{-1}, ω- and φ-scans, 44 365 measured intensities (3.6° ≤ 2θ ≤ 56.0°), semiempirical absorption correction (0.859 ≤ T ≤ 0.978), 7496 independent (R_{int} = 0.0450) and 5636 observed intensities ($I \geq 2\sigma(I)$), refinement of 405 parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions. R = 0.0312, wR = 0.0607, R_{all} = 0.0531, wR_{all} = 0.0653. The asymmetric unit contains one formula unit.

[**17**]. Crystals suitable for an X-ray diffraction study were obtained by slow evaporation of the solvent from a THF solution of [**17**]. $C_{36}H_{30}N_2O_3P_2W$, M = 784.41 g·mol^{-1}, colorless crystal, 0.46 × 0.16 × 0.06 mm^3, orthorhombic, space group *Pbca*, Z = 8, a = 16.766(3) Å, b = 16.528(3) Å, c = 22.564(5) Å, V = 6253(2) Å^3, ρ_{calc} = 1.667 g·cm^{-3}, μ = 3.837 mm^{-1}, ω- and φ-scans, 59 375 measured intensities (3.6° ≤ 2θ ≤ 55.9°), semiempirical absorption correction (0.271 ≤ T ≤ 0.802), 7398 independent (R_{int} = 0.0688) and 5348 observed intensities ($I \geq 2\sigma(I)$), refinement of 405 parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions. R = 0.0289, wR = 0.0603, R_{all} = 0.0493, wR_{all} = 0.0658. The asymmetric unit contains one formula unit.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic files for [**6**], [**6**]$_2$·2CH_2Cl_2, [**10**], [**13**]·THF, [**15**]·Et_2O, [**16**], and [**17**] (CIF files). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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