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Chemistry of highly electrophilic binuclear cations. 6. Synthesis of the alkyne-bridged complexes $[Mo_2(\eta^5\text{-}C_5H_5)_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}HC_2(p\text{-}tol)\}(CO)_2(\mu\text{-}L_2)][B\{3,5\text{-}C_6H_3(CF_3)_2\}_4]_2$ and their isocyanide derivatives ($L_2 = Ph_2PCH_2PPh_2$, $Me_2PCH_2PMe_2$)

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Abstract

One-electron oxidation of the alkyne-bridged radicals $[Mo_2Cp_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}HC_2(p\text{-}tol)\}(CO)_2(\mu\text{-}L_2)](BAr'_4)$ [$Cp = \eta^5 - C_5H_5$; L_2=$Ph_2PCH_2PPh_2$ (dppm), $Me_2PCH_2PMe_2$ (dmpm); $Ar' = 3,5\text{-}C_6H_3(CF_3)_2$] with the ferricenium salts $[FeCp_2]X$ ($X = BAr'^-_4$, BF^-_4) gives the dipositive cationic complexes $[Mo_2Cp_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}HC_2(p\text{-}tol)\}(CO)_2(\mu\text{-}L_2)](BAr'_4)(X)$ which display two isomeric geometries differing in the position (*cis* or *trans*) of the alkyne ligand relative to the diphosphine bridge, with the *cis* isomer being dominant for the dmpm complex and the reverse for the dppm derivative. These 32-electron complexes turned out to be quite stable and do not experience deprotonation, dehydrogenation or any rearrangement in the bonded alkyne even under heating. However, they react rapidly with CN^tBu at room temperature to give new isocyanide derivatives stepwise. Addition of one equivalent of CN^tBu leads to the monocarbonyl complexes $[Mo_2Cp_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}HC_2(p\text{-}tol)\}(CO)(CN^tBu)(\mu\text{-}L_2)](BAr'_4)_2$ (L_2 = dppm, dmpm) resulting from substitution of one carbonyl ligand. Addition of a second equivalent of isocyanide on the dmpm cation replaces the remaining carbonyl to give the diisocyanide complex $[Mo_2Cp_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}HC_2(p\text{-}tol)\}(CN^tBu)_2(\mu\text{-}dmpm)](BAr'_4)_2$, while a large excess of ligand forces the incorporation of a third isocyanide molecule to the unsaturated metal centre, to give the electron-precise triisocyanide derivative $[Mo_2Cp_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}HC_2(p\text{-}tol)\}(CN^tBu)_3(\mu\text{-}dmpm)](BAr'_4)_2$. The latter is a labile cation which dissociates isocyanide in solution at room temperature. All new compounds were characterized on the basis of their spectroscopic IR and NMR (^1H, ^{31}P, ^{13}C) data.

Keywords: Molybdenum; Alkyne ligands; Radical reactions; Metal–metal interactions; Lewis acids; Isocyanide ligands

1. Introduction

In the previous part of this series [1] we reported that the reactions of the 33-electron radicals $[Mo_2Cp_2(\mu\text{-}CO)_2(CO)_2(\mu\text{-}L_2)](BAr'_4)$ [$L_2 = Ph_2PCH_2PPh_2$ (dppm), $Me_2PCH_2PMe_2$ (dmpm); $Ar' = 3,5\text{-}C_6H_3(CF_3)_2$] with the 1-alkynes HCCR ($R = p$-tol, ^{t}Bu, CO_2Me) gives two main type of products, the diamagnetic dicarbonyls $[Mo_2Cp_2\{\mu\text{-}\eta^2\text{:}\eta^3\text{-}HCC(R)C(OH)\}(CO)_2(\mu\text{-}L_2)](BAr'_4)$ and the alkyne-bridged radicals $[Mo_2Cp_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}HC_2R\}(CO)_2(\mu\text{-}L_2)](BAr'_4)$, which are unexpectedly stable (Scheme 1). The latter complexes are of interest due to the scarce number of organometallic radicals available with metal–metal bonds of order higher than one [2,3], so that their chemistry remains largely unexplored. Since the above alkyne-bridged radicals were obtained in good yield when $R = p$-tol and proved to be stable enough to be properly isolated, they were suitable candidates for testing its reactivity and influence on the bonded alkyne ligand. We thus decided to explore in detail the chemical behaviour of the paramagnetic

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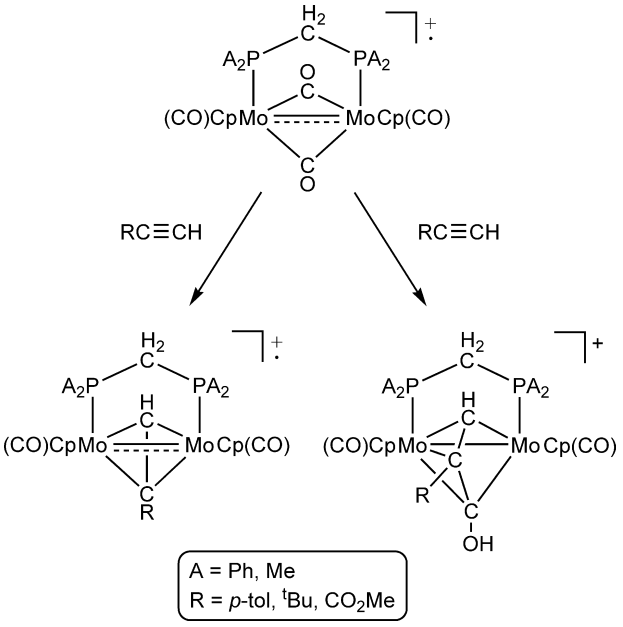


Scheme 1.

complexes $[Mo_2Cp_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}HC_2(p\text{-tol})\}(CO)_2(\mu\text{-}L_2)](BAr'_4)$ [μ-L_2 = dppm (**1a**), dmpm (**1b**)].

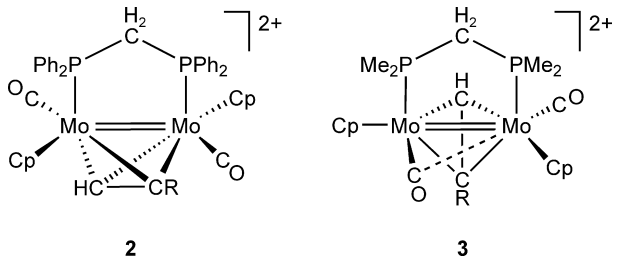
Some preliminary experiments revealed that compounds **1a,b** exhibit a surprising lack of reactivity, considering that they are electron-odd organometallic molecules. For example, they are not involved in typical radical reactions such as dehydrogenation, even under heating or UV irradiation. Deprotonation reactions do not occur easily either, even in the presence of strong bases; however, the alkyne ligand can be activated through reduction with Na amalgam, this unexpectedly inducing an H-atom transfer process in the bonded alkyne to give a new but unstable radical [1]. We then turned our attention to the oxidation reactions of compounds **1**, since these could lead to dipositive and unsaturated cations able to activate the alkyne ligand with respect to either deprotonation or other rearrangements. We have previously shown that the presence of multiple metal–metal bonds combined with high positive charges at binuclear transition–metal complexes enhances the Lewis acidity of the dinuclear centre and promotes novel transformations of interest [4–6]. In this paper we report our results on the oxidation reactions of radicals **1a,b** with $[FeCp_2]X$ [X = BF_4 and BAr'_4] and some reactivity studies of the resulting dipositive cations. As it will be shown, the latter turned to display low reactivity for such potentially highly electrophilic species, although carbonyl substitution by CN^tBu takes place easily at room temperature. In all these reactions, the alkyne ligand remains essentially unperturbed.

2. Results and discussion

2.1. One-electron oxidation of radicals *1*

Compound **1a** is readily oxidized with one equivalent of the ferricenium salt $[FeCp_2](BAr'_4)$ in dichloromethane to give almost quantitatively the purple diamagnetic dicarbonyl $[Mo_2Cp_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}HC_2(p\text{-tol})\}(CO)_2(\mu\text{-dppm})](BAr'_4)_2$ (**2**). In contrast, oxidation of the dmpm-bridged complex **1b** leads to a product of similar formula $[Mo_2Cp_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}HC_2(p\text{-tol})\}(CO)_2(\mu\text{-dmpm})](BAr'_4)_2$ (**3**), but very different colour (deep green). Spectroscopic data for the latter product (see below) in fact indicates that it displays two isomers in solution, in a 30:1 ratio, with the minor isomer (*trans*-**3**) being isostructural to **2**, and the major (green) isomer having the bridging alkyne ligand positioned *cis* to the phosphine bridge (Chart 1). The oxidation reactions using $[FeCp_2](BF_4)$ proceeded analogously to give the mixed salts $[Mo_2Cp_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}HC_2(p\text{-tol})\}(CO)_2(\mu\text{-}L_2)](BAr'_4)(BF_4)$ [**2′** (L_2 = dppm), **3′** (L_2 = dmpm)].

IR and NMR spectroscopic data for compounds **2** and **2′** (Table 1 and Section 3) indicate that they are isostructural to each other and firmly support the geometry proposed (Chart 1), with the diphosphine and alkyne bridges positioned *trans* to each other and the carbonyls and cyclopentadienyl centroids placed in a plane perpendicular to the average one defined by the bridges. The IR spectra show just one strong band in the region for terminal carbonyls, consistent with the presence of two CO ligands arranged in *trans* and almost antiparallel to each other [7]. This is confirmed through the ^{13}C NMR spectrum of **2**, which exhibits two doublets in the terminal carbonyl region, at 219.4 (J_{CP} = 15 Hz) and 216.1 ppm (J_{CP} = 12 Hz). The similar shieldings of these two resonances indicate that the chemical environments of the carbonyl ligands are very close to each other, which is consistent with the proposed structure since the only difference between the environments of both metal centres comes from the distinct substituents (H vs. *p*-tol) in the alkyne bridge. In line with this, the ^{31}P NMR spectra of both **2** and **2′**, display AB multiplets, and the cyclopentadienyl ligands give two slightly different resonances in the ^{13}C NMR spectra. As for the alkyne ligand, it gives rise to a very deshielded proton resonance displaying similar but low couplings to the P atoms (for salt **2**: δ = 9.59 ppm, J_{HP} = 2, 1.7 Hz), while the metal-bound carbon atoms give resonances at *ca.* 145 ppm (internal) and 109.8 ppm (terminal), in the upper part of the regions observed for electron-precise compounds of the type $[Mo_2Cp_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}RCCR')(CO)_4]$ [8,9].



2 **3**

Chart 1.

Table 1
IR and $^{31}P\{^1H\}$ NMR data for new compounds

Compound	ν_{st}(CO)[a]/cm^{-1}	ν_{st}(CN)[a]/cm^{-1}	δP[b]	J_{PP}
$[Mo_2Cp_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}HC_2(p\text{-tol})\}(CO)_2(\mu\text{-dppm})](BAr'_4)_2$ (**2**)	1950 (s)		48.4, 46.8	96
$[Mo_2Cp_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}HC_2(p\text{-tol})\}(CO)_2(\mu\text{-dppm})](BAr'_4)(BF_4)$ (**2′**)	1943 (s)		50.2, 48.4	99
$[Mo_2Cp_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}HC_2(p\text{-tol})\}(CO)_2(\mu\text{-dmpm})](BAr'_4)_2$ (**3**)	2039 (s), 1927 (vs)		29.0, 10.1[c,d]	28
$[Mo_2Cp_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}HC_2(p\text{-tol})\}(CO)_2(\mu\text{-dmpm})](BAr'_4)_2$ (*trans*-**3**)			30.2, 27.2[c,d]	88
$[Mo_2Cp_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}HC_2(p\text{-tol})\}(CO)_2(\mu\text{-dmpm})](BAr'_4)(BF_4)$ (**3′**)	2036 (sh, s), 2030 (s), 1933 (vs)		29.0, 10.5[d,e]	29
$[Mo_2Cp_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}HC_2(p\text{-tol})\}(CN^tBu)(CO)(\mu\text{-dppm})](BAr'_4)_2$ (**4a**)	1900 (vs)	2177 (s)	53.9, 33.6	37
$[Mo_2Cp_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}HC_2(p\text{-tol})\}(CN^tBu)(CO)(\mu\text{-dmpm})](BAr'_4)_2$ (**4b**)	1905 (vs)	2176 (s)	30.7, 11.1	33
$[Mo_2Cp_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}HC_2(p\text{-tol})\}(CN^tBu)_2(\mu\text{-dmpm})](BAr'_4)_2$ (**5**)		2165 (vs), 2102 (s)	25.5, 11.1	38
$[Mo_2Cp_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}HC_2(p\text{-tol})\}(CN^tBu)_3(\mu\text{-dmpm})](BAr'_4)_2$ (**6**)		2145 (s), 2135 (sh), 2108 (vs)	38.4, 4.9[d,f]	46

[a] Recorded in CH_2Cl_2 solution unless otherwise stated.
[b] Recorded at 121.50 MHz and 291 K in CD_2Cl_2 solution, unless otherwise stated; δ in ppm relative to external 85% aqueous H_3PO_4; J in Hertz.
[c] Recorded at 243 K.
[d] Recorded at 161.98 MHz.
[e] Recorded at 253 K.
[f] Recorded at 223 K.

Spectroscopic data for the mixed salt **2′** are similar to those of **2**, except that only one (instead of two) cyclopentadienyl resonance is observed in its ^1H NMR spectrum, which we interpret as an accidental degeneracy. The C–O stretching band appears 7 cm^{-1} lower in frequency than that for **2**, which is suggestive of the presence in solution of significant interaction between the cation and the BF_4^- anion. This interaction might well involve an H···F contact with the alkyne proton, since the corresponding resonances in **2** and **2′** differ considerably ($\Delta\delta = 1.01$ ppm).

As for the very major isomer (green) in compound **3**, its dicarbonyl nature is now readily apparent since its IR spectrum exhibits two strong and quite separated bands ($\Delta\nu = ca.$ 100 cm^{-1}) in the C–O stretching region (Table 1). The relative intensities of these bands are indicative of a transoid arrangement of the MoCp(CO) moieties with a relative angle between the CO groups close to 90° [7], and the large difference in energy suggests that one of the carbonyls might be bound in a semibridging fashion. This is confirmed by the appearance of two very separated carbonyl resonances in the ^{13}C NMR spectrum of **3**, a doublet at 259.0 ppm ($J_{CP} = 13$ Hz) and a broad singlet at 218.1 ppm, and therefore suggests that the structure of **3** must be very similar to that recently determined for the electron-precise complex $[Mo_2Cp_2\{\mu\text{-}\eta^2\text{:}\eta^3\text{-}HCC(^tBu)C(OH)\}(CO)_2(\mu\text{-dppm})](BAr'_4)$ [1], by just replacing the hydrocarbyl bridge in the latter by a bridging alkyne (Chart 1). This quite asymmetric arrangement of two otherwise similar carbonyl ligands seems to be caused by the presence of a bridging ligand (here the alkyne) roughly in the same plane of the carbonyls, apart from the cyclopentadienyl groups. This is a geometrical feature which has been previously confirmed crystallographically also in the methoxycarbyne complex $[W_2Cp_2(\mu\text{-}COMe)(CO)_2(\mu\text{-dppm})](BF_4)$ [4], and in its methylene derivative $[W_2Cp_2(\mu\text{-}CH_2)\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}C(OMe)CH_2\}(CO)_2(\mu\text{-dppm})](BF_4)$ [10]. All other ^{13}C NMR resonances observed for **3** are in full agreement with the structure proposed for the cation. Particularly, the alkyne resonances at 186.4 (μ-C) and 116.0 ppm (μ-CH) are comparable to those for compound **2** discussed above, and therefore in agreement with the proposed $\mu\text{-}\eta^2\text{:}\eta^2$ coordination.

Further evidence in **3** for the positioning of the alkyne as a $\mu\text{-}\eta^2\text{-}\eta^2$-bridge and *cis* to the diphosphine ligand comes from the relatively large H–P couplings displayed by the methyne proton ($\delta = 10.04$ ppm, $J_{HP} = 15,\ 8$ Hz), compared to those in **2** (*ca.* 2 Hz). It is well established that three-bond P–H couplings are strongly dependent on the dihedral angle (ϕ) defined by the bonds involved [11]. On this basis, we expect that P–H couplings for the methyne proton in **2** [ϕ(H–C–Mo–P) close to 100 °] should be smaller than those for an alkyne ligand placed *cis* to the diphosphine bridge, for which we can estimate ϕ(H–C–Mo–P) values of ca. 40° or 140° depending on the relative position of the CH group, close or away from the diphosphine ligand. However, on steric grounds we propose that the *p*-tol substituent is most probably placed away from the diphosphine bridge (Chart 1). In contrast, the very minor isomer *trans*-**3** has presumably the same geometry as compound **2**, since its characteristic methyne resonance displays also very low P–H couplings (2 Hz). Interestingly, the ditungsten analogue of compound **2** was found to exist in solution as a roughly equimolar mixture of two isomers, these having spectroscopic properties resembling respectively those of **2** and **3** [6]. In particular, the P–H couplings of the methyne proton were found to be 1.5 and 1.5 Hz for one isomer, and 12 and 10 Hz for the other one. Thus we conclude that the isomers displayed by that ditungsten compound can be identified respectively with the structures of **2** and the major isomer of **3**, respectively [12].

A further difference between the structures of these two types of isomers concerns their dynamic behaviour. Thus,

while compound **2** behaves as a stereochemically rigid molecule, compound **3** (and also **3′**) exhibits broad ^{1}H and ^{31}P NMR resonances at room temperature which become well resolved below *ca.* 253 K. Although we have not studied this matter in detail, there seems to be more than one dynamic rearrangement involved. For example, the aromatic protons of the *p*-tol group appear as four distinct multiplets at low temperature (see Section 3), which is indicative of slow rotation of this aromatic ring and perhaps of substantial steric congestion within the cation. As the temperature is raised, these resonances first broaden and then almost disappear in the baseline of the spectrum. At the same time, the cyclopentadienyl resonances at 5.70 and 5.39 ppm first broaden and then collapse into a very broad resonance, which suggests the presence of a second process, an incipient site exchange between the inequivalent metal centres. This is also suggested by the fact that the two doublets at 29.0 and 10.1 ppm present in the ^{31}P NMR spectrum of **3** when recorded at 243 K then become two very broad resonances at about the same positions at room temperature. Incidentally, we note that it is only at low temperatures that the proton or ^{31}P resonances are sharp enough to allow for the detection of the very minor isomer *trans*-**3**, of which only the methyne and phosphorus resonances can be unambiguously identified (Table 1 and Section 3).

As anticipated above, the spectroscopic data for compound **3′** (Table 1 and Section 3) are very similar to those of **3**, both concerning its dynamic behaviour and the presence of a minor isomer *trans*-**3′**, now even in lower relative proportion. It should be noted that the IR spectrum of salt **3′** exhibits an additional shoulder on the more energetic C–O stretching band, indicative of some anion-cation interaction. However, this interaction seems to be weaker than that found in **2**, since the spectra of **3** and **3′** exhibit no substantial differences in their ^{1}H or ^{31}P chemical shifts.

2.2. Reactivity of compounds 2 and 3

Due to the high positive charge and electronic unsaturation present in complexes **2** and **3**, they were expected to be very reactive electrophiles. Surprisingly, these cations turned out to be rather stable. For instance, even when the high proton chemical shifts of the corresponding methyne groups might anticipate high acidity, these turned to be unexpectedly resistant to deprotonation. Indeed, treatment of cations **2** and **3** with different bases (such as DBU, KOH or Na_2CO_3) led directly to the corresponding starting radicals **1**. Decarbonylation reactions were also performed in order to get more unsaturated cations which could perhaps induce further rearrangements in the bonded alkyne. Although no reaction was observed when complexes **2** or **3** were heated in refluxing THF, decarbonylation was induced under UV–visible light irradiation, but it was not possible to achieve a satisfactory control of the process. An intermediate species exhibiting just one ν(CO) band at ca. 1900 cm^{-1} was detected using short photolysis times, but it would decompose just by removal of solvent from the reaction mixture; thus it was thought to be a solvate complex of the type $[Mo_2Cp_2(\mu\text{-}HC_2R)(CO)(THF)(\mu\text{-}L_2)]^{2+}$. In order to verify this hypothesis, we examined the reactions of **2** and **3** with CN^tBu, which turned out to proceed easily at room temperature without photochemical activation, this being now more consistent with the electron-deficient nature of these complexes. However, the products formed in these reactions were strongly dependent on the available amount of isocyanide ligand, as it will be discussed next.

2.3. Reaction of 2 and 3 with 1 equivalent of CN^tBu

Compounds **2** and **3** react readily with stoichiometric amounts of CN^tBu at room temperature to give the monocarbonyl cations $[Mo_2Cp_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}HC_2(p\text{-tol})\}(CN^tBu)(CO)(\mu\text{-}L_2)](BAr'_4)_2$ [L_2 = dppm (**4a**), dmpm (**4b**)] in good yields. Spectroscopic data for both complexes are very similar (Table 1 and Section 3) and so are their colours, deep green in both cases. This indicates that both monocarbonylic complexes have the same structure, now being independent of the diphosphine ligand present, contrary to that found for the dicarbonyls **2** and **3**.

The spectroscopic data for compounds **4** (including their colour) clearly suggest a structure derived from that of **3**, by just replacing that carbonyl pointing away from the dimetal centre (less sterically demanding position) by a terminal isocyanide ligand (Chart 2). Indeed, the slightly semibridging nature of the remaining carbonyl ligand in these molecules is clearly indicated by its relatively low (for a dipositive cation) C-O stretching frequency (*ca.* 1900 cm^{-1}), and quite deshielded ^{13}C NMR resonance (265.1 ppm for **4a**). As for the isocyanide ligand, its terminal coordination in compounds **4** is warranted by the high C–N stretching frequencies in the IR spectra (*ca.* 2176 cm^{-1}), and relatively low ^{13}C chemical shifts of the metal-bound carbon atom (147.0 ppm for **4a**). The $^{31}P\{^{1}H\}$ NMR spectra of compounds **4** are also in agreement with the asymmetric structure proposed for these cations, both showing two resonances differing by some 20 ppm, as found for the major isomer in **3**. As for the alkyne ligand, it gives ^{1}H and ^{13}C NMR resonances similar to those measured in **3**. In particular, the methyne proton in compounds **4** displays high P–H couplings (*ca.* 14 Hz) to both phosphorus atoms, consistent with the coordina-

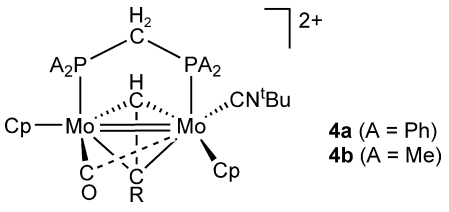


Chart 2.

tion of the alkyne ligand *cis* to the diphosphine bridge (see Section 3).

The selective formation of *cis* isomers for complexes **4** from either the *trans* (**2**) or *cis* (**3**) structures, leads us to conclude that electronic factors are dominant at defining the most stable isomer. In the case of the dicarbonyls **2** and **3**, the *trans* isomer (relative positions of alkyne and diphosphine) is dominant for the bulkier and better acceptor diphosphine (dppm) while the *cis* isomer is dominant for the smaller and better donor diphosphine (dmpm). Replacing a CO ligand by CN^{t}Bu (a better donor but much bulkier ligand than CO) clearly increases both the electron density and the steric crowding at the dimetal centre; yet only the *cis* isomer is observed, which thus seems to be favoured upon increasing electron density at the metals, despite of unfavourable steric crowding. Under this assumption, further replacement of CO by CN^{t}Bu should lead to only *cis* isomers, as confirmed in the case of **4a**, next discussed.

2.4. Reaction of 3 with excess of CN^{t}Bu

Complex **3** reacts with two equivalent of CN^{t}Bu at room temperature to give the diisocyanide derivative [$Mo_2Cp_2\{\mu$-η^2:η^2-$HC_2(p\text{-tol})\}(CN^tBu)_2(\mu\text{-dmpm})](BAr'_4)_2$ (**5**), along with small amounts of the triisocyanide complex [$Mo_2Cp_2\{\mu$-η^2:η^2-$HC_2(p\text{-tol})\}(CN^tBu)_3(\mu\text{-dmpm})](BAr'_4)_2$ (**6**), (Chart 3). The formation of the latter requires the addition of a third isocyanide molecule to the dimetal centre, a reaction possible due to the presence of a slight excess of ligand in the reaction mixture. Indeed, when this reaction mixture is treated with an excess of CN^{t}Bu, compound **6** becomes the major species in solution, although a small amount of **5** always remains present, which suggests a dissociative behaviour of **6**. Indeed, although the latter complex is electronically saturated, it releases spontaneously a molecule of isocyanide to regenerate compound **5** as soon as the excess of ligand is removed from the medium (for example, when removing solvents under vacuum). As a result, compound **6** could not be isolated as a pure solid, and its spectroscopic characterization had to be done in presence of an excess of isocyanide and at low temperature. This dissociative behaviour of **6** can be interpreted as an indicator of severe steric crowding in the cation, which is considerably relieved when an isocyanide molecule is released. It also gives a model for the reaction pathway

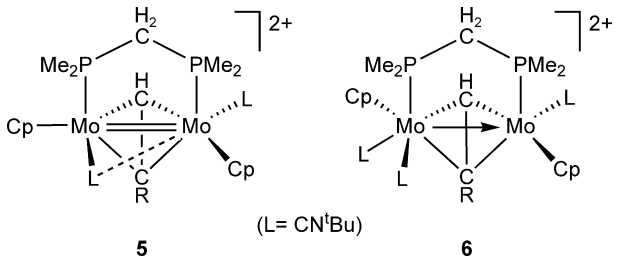


Chart 3.

likely operative in the formation of compounds **4** and **5**, that is, isocyanide addition to the unsaturated substrate followed by irreversible dissociation of carbon monoxide. On the other hand, compound **5** is not a stable compound either, and all attempts to obtain it as a pure material or in crystalline form led to its progressive decomposition. Therefore, its spectroscopic characterization also had to be done directly from reaction mixtures.

The IR spectrum of **5** displays two C–N stretching bands in the region of terminal isocyanide ligands (Table 1). Moreover, their similar relative intensities and large separation indicate that this compound retain a transoid arrangement of these terminal ligands, as found in the dicarbonyl **3** and the carbonyl-isocyanide compounds **4**. In the case of **5** this results from the presence of one of the CNR ligands pointing away from the dimetal centre while the second isocyanide is lining over the metal–metal vector, in a semibridging fashion (hence the relatively large frequency separation), therefore defining and angle between CNR groups close to 90° (hence the similar intensities for the C–N stretching bands [7]). In agreement with this, the ^{31}P NMR spectrum exhibits quite separated resonances for the inequivalent phosphorus nuclei ($\Delta\delta = 24$ ppm) and the ^{1}H NMR spectrum shows a methyne resonance strongly deshielded and displaying high P–H couplings to the diphosphine ($\delta = 9.34$ ppm, $J_{PH} = 14$, 12 Hz). This is a characteristic feature of these cations having the alkyne bridge positioned *cis* to the diphosphine ligand, as it is the slow rotation of the *p*-tol substituent of the alkyne, also found for **5** (see Section 3).

In contrast, the spectroscopic data for compound **6** indicates that the coordination of a third isocyanide molecule causes a significant departure from the structure found in compounds **3** to **5**. Somewhat unexpectedly, the three CN^{t}Bu ligands adopt a terminal coordination mode, as indicated by their high C–N stretches (Table 1) and ^{13}C NMR resonances at 167.0, 164.4 and 152.2 ppm. However, the resonances for the metal-bound carbon atoms in the alkyne ligand, a singlet at 102.2 ppm for the internal carbon atom and a triplet with $J_{PC} = 18$ Hz at 89.0 ppm for the terminal carbon atom, are considerably shielded when compared to the related resonances in the unsaturated complexes **4b** and **5**. Yet, the high P–C couplings of the latter resonance suggest a symmetrically bridging position for the CH moiety, *cis* to the phosphorus atoms, since the absolute values of $^2J_{PC}$ couplings in complexes of the type [$MCpX(CO)_2(PR_3)$] (M = Mo, W; X = halogen, alkyl, hydride, etc) usually follow the order $J_{cis} > J_{trans}$ [13]. In agreement with this, the CH resonance of the bridging alkyne ligand now appears considerably more shielded ($\delta = 5.54$ ppm), but here the couplings to the phosphorus atoms are quite different ($J_{HP} = 15$, 4 Hz), suggesting a more asymmetric coordination of the alkyne ligand to the dimetal centre, which perhaps would compensate for the distinct number of isocyanide ligands bonded to the molybdenum atoms. There are many possibilities for asymmetric binding of an alkyne ligand to a dimetal centre [10,14–16],

and our spectroscopic data do not allow us to fully identify the actual coordination mode of the alkyne bridge in **6**. Thus, the structural diagram depicted in Chart 3 must be considered only as an oversimplified representation of this unstable cation.

3. Experimental

All reactions were carried out under an atmosphere of nitrogen. Solvents were purified according to standard procedures [17], and distilled under nitrogen prior to use. Petroleum ether refers to that fraction distilling in the range 65–70 °C. Compounds **1a** and **1b** were prepared as reported before [1], and the reagents $[FeCp_2]BF_4$ and $[FeCp_2](BAr'_4)$ were also prepared by literature procedures [18,19]. All other reagents were purchased from the usual commercial suppliers and used as received. NMR spectra were recorded at 300.13 (^1H), 100.61 ($^{13}C\{^1H\}$) or 121.50 MHz ($^{31}P\{^1H\}$) in CD_2Cl_2 at room temperature, unless otherwise indicated. Chemical shifts (δ) are given in ppm, relative to internal TMS (^1H, ^{13}C) or external 85% H_3PO_4 aqueous solution (^{31}P), with positive values for frequencies higher than that of the reference. Coupling constants (J) are given in Hertz. $^{13}C\{^1H\}$ NMR spectra were routinely recorded on solutions containing a small amount of tris(acetylacetonato)chromium (III) as a relaxation reagent.

3.1. Preparation of $[Mo_2Cp_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}HC_2(p\text{-}tol)\}(CO)_2(\mu\text{-}dppm)](BAr'_4)_2$ (**2**)

Solid $[FeCp_2](BAr'_4)$ (0.021 g, 0.020 mmol) was added to a dichloromethane solution (8 mL) of compound **1a** (0.035 g, 0.020 mmol), whereupon the green solution changed instantaneously to purple. Stirring was continued for 15 min and then the solvent was removed under vacuum. The solid residue was washed with petroleum ether (3×10 mL) to give compound **2** as a purple microcrystalline powder (0.049 g, 92%). Anal. Calc. for $C_{110}H_{64}B_2F_{48}Mo_2O_2P_2$: C, 50.72; H, 2.48. Found: C, 50.62; H, 2.48%. ν(C=C) (CH_2Cl_2): 1602 (w) cm^{-1}. ^1H NMR: δ 9.59 (dd, $J_{HP} = 2$, 1.7, 1H, CH), 7.72 (s, 16H, Ar′), 7.55 (s, 8H, Ar′), 7.66–7.30 (m, 24H, Ph, *p*-tol), 5.36, 5.35 ($2 \times$ s, 2×5H, Cp), 4.89, 4.74 ($2 \times$ m, ABMX, 2×1H, CH_2), 2.49 (s, 3H, Me) ppm. $^{13}C\{^1H\}$ NMR (50.32 MHz): δ 219.4 (d, $J_{CP} = 15$, CO), 216.1 (d, $J_{CP} = 12$, CO), 162.6 [q, $J_{CB} = 50$, C^1(Ar′)], 146.6, 144.9 [$2 \times$ s, C^1(*p*-tol) and HC*C*(*p*-tol)], 139.9 [s, C^4(*p*-tol)], 134.7-117.3 (Ph), 135.6 [s, C^2(Ar′)], 129.7 [q, $J_{CF} = 32$, C^3(Ar′)], 125.4 [q, $J_{CF} = 272$, CF_3], 118.3 [s, C^4(Ar′)], 109.8 [s, H*C*C(*p*-tol)], 100.5, 99.9 ($2 \times$ s, Cp), 44.6 (t, $J_{CP} = 28$, CH_2), 22.1 (s, C_6H_4Me) ppm.

3.2. Preparation of $[Mo_2Cp_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}HC_2(p\text{-}tol)\}(CO)_2(\mu\text{-}dppm)](BAr'_4)(BF_4)$ (**2′**)

The procedure is completely analogous to that described for **2**, except that $[FeCp_2](BF_4)$ (0.006 g, 0.020 mmol) was used instead. Compound **2′** is thus obtained as a purple microcrystalline powder (0.034 g, 90%). Anal. Calc. for $C_{78}H_{52}B_2F_{28}Mo_2O_2P_2$: C, 51.23; H, 2.87. Found: C, 51.20; H, 2.88%. ν(C=C) (CH_2Cl_2): 1602 (w) cm^{-1}. ^1H NMR: δ 10.61 (s, 1H, CH), 7.71 (s, 8H, Ar′), 7.54 (s, 4H, Ar′), 7.66–7.10 (m, 24H, Ph, *p*-tol), 5.40 (s, 10H, Cp), 4.91, 4.69 ($2 \times$ m, ABMX, 2×1H, CH_2), 2.53 (s, 3H, Me) ppm.

3.3. Preparation of $[Mo_2Cp_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}HC_2(p\text{-}tol)\}(CO)_2(\mu\text{-}dmpm)](BAr'_4)_2$ (**3**)

Solid $[FeCp_2](BAr'_4)$ (0.025 g, 0.023 mmol) was added to a dichloromethane solution (8 mL) of compound **1b** (0.035 g, 0.023 mmol), whereupon the green solution changed instantaneously to blue-green. Stirring was continued for 15 min and then the solvent was removed under vacuum. The solid residue was washed with petroleum ether (3×10 mL) to give compound **3** as a green microcrystalline powder (0.048 g, 88%). This solid contains a very small amount of a second isomer (*trans*-**3**) in a ratio 1:30. Anal. Calc. for $C_{90}H_{56}B_2F_{48}Mo_2O_2P_2$: C, 45.87; H, 2.40. Found: C, 45.77; H, 2.47%. ν(C=C) (CH_2Cl_2): 1599 (w) cm^{-1}. ^1H NMR (400.14 MHz, 223 K): δ 10.04 (dd, $J_{HP} = 15$, 8, 1 H, CH), 8.30, 7.47, 7.18, 5.72 ($4 \times$ d, $J_{HH} = 8$, 4×1H, C_6H_4), 7.79 (s, 16H, Ar′), 7.61 (s, 8H, Ar′), 5.70 (d, $J_{HP} = 1.6$, 5H, Cp), 5.39 (d, $J_{HP} = 2$, 5H, Cp), 3.50 (dt, $J_{HH} = 12$, $J_{HP} = 15$, 1H, CH_2), 2.80 (ddd, $J_{HH} = 12$, $J_{HP} = 15$, 10, 1H, CH_2), 2.35 (s, 3H, C_6H_4-*Me*), 1.69, 1.56, 1.45 ($3 \times$ d, $J_{HP} = 10$, 3×3H, Me), 1.57 (d, J_{HP}=9, 3H, Me) ppm. Data for *trans*-**3**: $\delta = 9.50$ (*t*, $J_{HP} = 2$, 1H, CH) ppm. The remaining signals for this minor isomer were obscured by those of the major isomer. $^{31}P\{^1H\}$ NMR: δ 28.2 (br s, μ-dmpm), 9.4 (br s, μ-dmpm) ppm. $^{31}P\{^1H\}$ NMR (161.98 MHz, CD_2Cl_2, 243 K): δ 30.2, 27.2 [AB, $J_{PP} = 88$, *trans*-**3**], 29.0 [d, $J_{PP} = 29$, main isomer], 10.1 [d, $J_{PP} = 29$, main isomer] ppm. $^{13}C\{^1H\}$ NMR (50.32 MHz, 213 K): δ 259.0 (d, $J_{CP} = 13$, CO), 218.1 (br s, CO), 186.4 [s, HC*C*(*p*-tol)], 162.0 [q, $J_{CB} = 50$, C^1(Ar′)], 146.9, 144.1 [$2 \times$ s, C^1(*p*-tol) and C^4(*p*-tol)], 134.9 [s, C^2(Ar′)], 134.0, 131.6, 129.9, 122.8 ($4 \times$ s, C_6H_4), 128.8 [q, J_{CF}=32, C^3(Ar′)], 124.5 [q, $J_{CF} = 272$, CF_3], 117.7 [s, C^4(Ar′)], 116.0 [br s, H*C*C(*p*-tol)], 98.7, 97.4 ($2 \times$ s, Cp), 50.6 (t, $J_{CP} = 34$, CH_2), 21.5 (s, C_6H_4*Me*), 20.6 (d, $J_{CP} = 34$, Me), 20.1 (d, J_{CP}=31, $2 \times$ Me), 18.0 (d, $J_{CP} = 31$, Me) ppm.

3.4. Preparation of $[Mo_2Cp_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}HC_2(p\text{-}tol)\}(CO)_2(\mu\text{-}dmpm)](BAr'_4)(BF_4)$ (**3′**)

The procedure is completely analogous to that described for **3**, except that $[FeCp_2](BF_4)$ (0.006 g, 0.023 mmol) was used instead. Compound **3′** is thus obtained as a blue-green microcrystalline powder (0.034 g, 92%). Anal. Calc. for $C_{58}H_{44}B_2F_{28}Mo_2O_2P_2$: C, 44.08; H, 2.81. Found: C, 44.15; H, 2.89%. ν(C=C) (CH_2Cl_2): 1604 (w) cm^{-1}. ^1H NMR (400.14 MHz, 223 K): δ 10.28 (dd, $J_{HP} = 15$, 8,

1H, CH), 8.36, 7.49, 7.18, 5.75 (4 × d, $J_{HH} = 8$, 4 × 1H, C_6H_4), 7.81 (s, 8H, Ar′), 7.62 (s, 4H, Ar′), 5.67, 5.38 (2 × s, 2 × 5H, Cp), 3.68 (q, $J_{HH} = J_{HP} = 13$, 1H, CH_2), 2.76 (dt, $J_{HH} = 13$, $J_{HP} = 11$, 1H, CH_2), 2.36 (s, 3H, C_6H_4*Me*), 1.67 (d, $J_{HP} = 9$, 3H, Me), 1.55 (d, $J_{HP} = 9$, 6H, Me), 1.43 (d, $J_{HP} = 9$, 3H, Me) ppm. $^{31}P\{^1H\}$ NMR (161.98 MHz): $\delta = 28.5$ (br s, μ-dmpm), 9.8 (br s, μ-dmpm) ppm.

3.5. Preparation of [$Mo_2Cp_2\{\mu$-η^2:η^2-HC_2(*p*-tol)}(CN^{t}Bu)(CO)(μ-dppm)](BAr′$_4$)$_2$ (**4a**)

A solution of CN^{t}Bu (223 μl of a 0.05 M solution in petroleum ether, 0.012 mmol) was added to a dichloromethane solution (8 mL) of compound **2** (0.032 g, 0.012 mmol), whereupon the purple solution changed instantaneously to green. Stirring was continued for 15 min and then the solvent was removed under vacuum. The solid residue was washed with petroleum ether (2 × 10 mL) to give compound **4a** as a green microcrystalline powder (0.029 g, 88%). Anal. Calc. for $C_{114}H_{73}B_2F_{48}Mo_2NOP_2$: C, 51.47; H, 2.77. Found: C, 51.42; H, 2.75%. ^1H NMR: δ 10.14 (t, $J_{HP} = 14$, 1H, CH), 7.76 (s, 16H, Ar′), 7.59 (s, 8H, Ar′), 7.51–6.96 (m, 24H, Ph, *p*-tol), 5.48 (d, $J_{HP} = 1$, 5H, Cp), 4.99 (d, $J_{HP} = 2$, 5H, Cp), 4.47 (t, $J_{HP} = 11$, 2H, CH_2), 2.47 (s, 3H, C_6H_4*Me*), 1.10 (s, 9H, ^{t}Bu) ppm.$^{13}C\{^1H\}$ NMR: δ 265.1 (d, $J_{CP} = 13$, CO), 184.2 [s, HC*C*(*p*-tol)], 161.9 [q, $J_{CB} = 50$, C^1(Ar′)], 147.0 (d, $J_{CP} = 14$, *C*N^{t}Bu), 145.4, 143.6 [2 × s, C^1(*p*-tol) and C^4(*p*-tol)], 134.8 [s, C^2(Ar′)], 134.4–122.5 (Ph), 131.3, 125.0 (2 × s, C_6H_4Me), 128.8 [q, $J_{CF} = 31$, C^3(Ar′)], 124.6 [q, $J_{CF} = 272$, CF_3], 118.0 (br s, H*C*C(*p*-tol)], 117.7 [s, C^4(Ar′)], 100.5, 97.4 (2 × s, Cp), 61.8 (m, CH_2), 61.5 [s, C^1(^{t}Bu)], 28.9 [s, C^2(^{t}Bu)], 21.5 (s, C_6H_4*Me*) ppm.

3.6. Preparation of [$Mo_2Cp_2\{\mu$-η^2:η^2-HC_2(*p*-tol)}(CN^{t}Bu)(CO)(μ-dmpm)](BAr′$_4$)$_2$ (**4b**)

The procedure is completely analogous to that described for **4a**, except that compound **3** (0.029 g, 0.012 mmol) was used instead. Compound **4b** was thus obtained as a green microcrystalline powder (0.026 g, 87%). Anal. Calc. for $C_{94}H_{65}B_2F_{48}Mo_2NOP_2$: C, 46.81; H, 2.72. Found: C, 46.77; H, 2.70%. ^1H NMR: δ 9.59 (dd, $J_{HP} = 16$, 11, 1H, CH), 7.72 (s, 16H, Ar′), 7.56 (s, 8H, Ar′), 5.65 (d, $J_{HP} = 1$, 5H, Cp), 5.14 (d, $J_{HP} = 3$, 5H, Cp), 3.40 (dt, $J_{HH} = 15$, $J_{HP} = 12$, 1H, CH_2), 2.74 (dt, $J_{HH} = 15$, $J_{HP} = 10$, 1H, CH_2), 2.35 (s, 3H, C_6H_4*Me*), 1.60 (d, $J_{HP} = 10$, 3H, Me), 1.51, 1.43, 1.31 (3 × d, J_{HP}=9, 3 × 3H, Me), 1.25 (s, 9H, ^{t}Bu) ppm.

3.7. Preparation of [$Mo_2Cp_2\{\mu$-η^2:η^2-HC_2(*p*-tol)}(CN^{t}Bu)$_2$(μ-dmpm)](BAr′$_4$)$_2$ (**5**)

A solution of CN^{t}Bu (446 μl of a 0.05 M solution in petroleum ether, 0.024 mmol) was added to a dichloromethane solution (8 mL) of compound **3** (0.029 g, 0.012 mmol). The green solution changed instantaneously to brownish-green, it was stirred for 20 min and then the solvent was removed under vacuum. The ^{31}P spectrum of the crude product indicated the presence of compound **5** as the major species, along with small amounts of compound **6**. However, compound **5** could not be isolated as a pure crystalline solid, since all attempts of crystallization or purification led to its progressive decomposition. ^1H NMR: δ 9.34 (dd, $J_{HP} = 14$, 12, 1H, CH), 7.72 (s, 16H, Ar′), 7.56 (s, 8H, Ar′), 5.28 (d, $J_{HP} = 1$, 5H, Cp), 4.97 (d, J_{HP}=2, 5H, Cp), 3.30 (dt, $J_{HH} = 15$, J_{HP}=12, 1H, CH_2), 2.43 (dt, J_{HH}=15, $J_{HP} = 10$, 1H, CH_2), 2.38 (s, 3H, C_6H_4*Me*), 1.91, 1.21 (2 × s, 2 × 9H, ^{t}Bu), 1.60, 1.34, 1.31 (3 × d, $J_{HP} = 9$, 3 × 3H, Me), 1.25 (d, $J_{HP} = 12$, 3H, Me) ppm. Signals due to H atoms of the *p*-tol ring could not be identified in this spectrum. ^1H NMR (400.14 MHz, 223 K): δ 9.32 (dd, $J_{HP} = 14$, 12, 1H, CH), 8.22, 7.43, 7.11, 5.89 (4 × d, $J_{HH} = 8$, 4 × 1H, C_6H_4), 7.78 (s, 16H, Ar′), 7.61 (s, 8H, Ar′), 5.26 (d, $J_{HP} = 1$, 5H, Cp), 5.01 (d, $J_{HP} = 2$, 5H, Cp), 3.33 (dt, $J_{HH} = 15$, $J_{HP} = 12$, 1H, CH_2), 2.44 (dt, $J_{HH} = 15$, $J_{HP} = 11$, 1H, CH_2), 2.37 (s, 3H, C_6H_4*Me*), 1.91, 1.22 (2 × s, 2 × 9H, ^{t}Bu), 1.35 (d, $J_{HP} = 8$, 3H, Me), 1.33, 1.25 (2 × d, J_{HP}=9, 2 × 3H, Me) ppm. The signal of one methyl group from the dmpm ligand could not be located in the spectrum, being possibly obscured by other signals in the region 1.75–1.45 ppm.

3.8. Preparation of solutions of compound [$Mo_2Cp_2\{\mu$-η^2:η^2-HC_2(*p*-tol)}(CN^{t}Bu)$_3$(μ-dmpm)](BAr′$_4$)$_2$ (**6**)

A great excess of CN^{t}Bu (0.8 ml of a 0.05 M solution in petroleum ether, 3.581 mmol) was added to a dichloromethane solution (8 mL) of compound **3** (0.029 g, 0.012 mmol). The green solution changed instantaneously to brown. Stirring was continued for 20 min and the brown solution thus obtained was shown (by NMR) to contain compound **6** as the major species. However, all attempts to isolate this complex (removal of solvent, crystallization, etc) led to spontaneous loss of CN^{t}Bu. ^1H NMR: δ 7.72 (s, 16H, Ar′), 7.56 (s, 8H, Ar′), 7.25 (s, 4H C_6H_4), 5.54 (dd, $J_{HP} = 15$, 4, 1H, CH), 4.96 (d, $J_{HP} = 2$, 5H, Cp), 4.93 (d, $J_{HP} = 3$, 5H, Cp), 2.74 (dt, J_{HH}=13, J_{HP}=12, 1H, CH_2), 2.37 (s, 3H, C_6H_4*Me*), 1.83, 1.67, 1.50 (3 × d, $J_{HP} = 8$, 3 × 3H, Me), 1.55, 1.54, 0.98 (3 × s, 3 × 9H, ^{t}Bu), 1.44 (dd, $J_{HP} = 7$, 2, 3H, Me), 1.06 (dt, $J_{HH} = 13$, J_{HP}=9, 1H, CH_2) ppm. ^1H NMR (400.14 MHz, 223 K): δ 7.78 (s, 16H, Ar′), 7.61 (s, 8H, Ar′), 7.23 (s, 4H, C_6H_4), 5.49 (dd, $J_{HP} = 15$, 4, 1H, CH), 4.96 (d, $J_{HP} = 3$, 5H, Cp), 4.94 (d, $J_{HP} = 2$, 5H, Cp), 2.78 (dt, J_{HH}=13, $J_{HP} = 12$, 1H, CH_2), 2.36 (s, 3H, C_6H_4*Me*), 1.86, 1.67, 1.51 (3 × d, $J_{HP} = 8$, 3 × 3H, Me), 1.56, 1.54, 0.94 (3 × s, 3 × 9H, ^{t}Bu), 1.46 (d, $J_{HP} = 7$, 3H, Me), 1.03 (dt, $J_{HH} = 13$, $J_{HP} = 10$, 1H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (223K): δ 167.0 (d, $J_{CP} = 28$, *C*N^{t}Bu), 164.4 (d, $J_{CP} = 13$, *C*N^{t}Bu), 162.2 [q, $J_{CB} = 50$, C^1(Ar′)], 152.2 (d, $J_{CP} = 26$, *C*N^{t}Bu), 140.8, 137.3 [2 × s, C^1(*p*-tol) and C^4(*p*-tol)], 135.1 [s, C^2(Ar′)], 133.6, 131.0 (2 × s, C_6H_4), 129.0 [q, $J_{CF} = 31$, C^3(Ar′)], 124.7 [q,

$J_{CF} = 272$, CF_3], 117.9 [s, $C^4(Ar')$], 102.2 [s, HC*C*(*p*-tol)], 95.2, 90.7 (2 × s, Cp), 89.0 (t, $J_{CP} = 18$, H*C*C(*p*-tol)], 61.1, 60.6, 59.4 [3 × s, $C^1(^tBu)$], 40.6 (dd, $J_{CP} = 38$, 15, CH_2), 30.7, 30.6, 29.7 [3 × s, $C^2(^tBu)$], 21.2 (s, C_6H_4*Me*), 19.8, 19.5 (2 × m, Me), 17.1, 17.0 (2 × d, $J_{CP} = 29$, Me) ppm.

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