Fixation of Metallo Nitrile Ylides and Metallo Nitrile Imines as Ligands in Transition Metal Complexes [1]

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Abstract. 1,3-Dipoles of the type metallo nitrile ylide and metallo nitrile imine were prepared by mono- α -deprotonation of CH-acidic {[W(CO)₅CHCH₂PPh₃]PF₆, *M*(CO)₅CNCH₂CO₂*R* (*M* = Cr, W; *R* = Me, Et), [Pt(Cl)(CNCH₂CO₂Et)(PPh₃)₂]BF₄} and NH-acidic isocyanide complexes (Cr(CO)₅CNNH₂) and were stabilized by coordination to a second transition metal complex fragment {Cr(CO)₅, [*M*(CO)₅]⁺ (*M* = Mn, Re), [FeCp(CO)₂]⁺, [Pt(Cl)(PR₃)₂]⁺ (*R* = Et, Ph)}. All dinu-

Introduction

Organic 1,3-dipoles of the nitrile ylide and nitrile imine type as a rule are unstable species eluding isolation [2]. Even so, their generation in the presence of a dipolarophile as reaction partner has led to a rich [3+2]-cycloaddition chemistry, which is inseparably bound up with the name of *Huisgen* [3]. However, using the right set of substituents, stable variants of both nitrilium betaïns such as **A** or **B** could be obtained [2c, 4, 5]. There is a review on stable nitrile imines [5b], and there are reports on the parent species $HC\equiv N^+-C^-H_2$ and $H-C\equiv N^+-N^-H$, which display a surprising stability in the gas phase [6, 7]. An overall view of their chemical ambience, derivation and interrelations also with isocyanides and isocyanide complexes has been presented recently [8].

Essentially the same picture can be painted in the case of metallo nitrile ylides **C** and imines **D**. In these organometallic versions of 1,3-dipoles, which have been studied by us for many years, the organyl substituent at the divalent carbon is replaced by a metal (or metalloid) complex fragment [9, 10]. Both, metallo nitrile ylides and metallo nitrile imines are basically accessible by deprotonation of the respective metal-coor-

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 $[(Ph_3P)_2(Cl)Pt{\mu_2-CNCH(CO_2Et)}Pt(Cl)(PPh_3)_2]BF_4 (8). Complex (OC)_5W{\mu_2-CNCH(CO_2Et)}Pt(Cl)(PEt_3)_2 (5b) was characterized by X-ray diffraction. Twofold deprotonation/platination to give (OC)_5Cr{\mu_3-CNC(Ph)}[Pt(Cl)(PPh_3)_2]_2 (9) was achieved in the case of Cr(CO)_5CNCH_2Ph.$

clear products 1-7, 10, and 11 are neutral species except

dinated α -CH- and -NH-acidic functional isocyanides. In no case, however, we were able to isolate the salt-like species cat⁺[$M{C=N^+-X^-}(CO)_5$]⁻ (cat⁺ = alkali or ammonium cation; X = CHR, NH) as a pure substance, nor could we get hold of neutral complexes such as [Pt{C=N^+-C^-HR}(Cl)(PPh_3)_2] ($R = CO_2Et$) [11]. Still, it proved sufficient to run their [3+2]-cy-cloaddition reactions with dipolarophiles "in situ", just like with the purely organic derivatives. Stable variants of C, which carry a PPh_3⁺ group at the trivalent carbon (E) could be obtained starting from a triphenylphosphonio-substituted methylisocyanide [9c, 9d, 12]. With some reservation – the primary cycloaddition product lacks the possibility of stabilization through H⁺ migration – the same applies to F [13].



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In this paper we report on the stabilization of the organometallic 1,3-dipoles by coordination to a second transition metal by the markedly negative α -C respectively α -N ends of the deprotonated functional isocyanides ethyl isocyanoacetate and isodiazomethane.

To the best of our knowledge no attempts to stabilize organic nitrile ylides or nitrile imines by metal coordination have so far been made.

Results and Discussion

1. Isocyanomethylenephosphorane as a C,C'-Bridging Ligand between $W(CO)_5$ and $Cr(CO)_5$ Entities

 $(OC)_5M^--C\equiv N^+-C^-(H)P^+Ph_3$ (M = Cr, W) proved to be the first stable metallo nitrile ylides just like CN-C⁻H-P⁺Ph₃ was the first stable α -carbanionic (or deprotonated, respectively, metalated) isocyanide [9c, 12]. The reaction of the tungsten complex with Cr(CO)₅THF to give 1 was studied with the objective to learn about its coordination potential through the vlidic carbon atom. Numerous transition metal complexes of Pylides have been described; due to the stabilizing effect of metal coordination one could even get hold of several reactive intermediates [14-19]. In solution, however, these complexes turn out to be rather unstable reverting to the components and further degradation products [20, 21]. This behavior is also shown by 1, which in THF or CH₂Cl₂ mainly suffers hydrolysis to give W(CO)5CNMe and triphenylphosphane oxide. Two sets of the v(CO) band pattern characteristic of $M(CO)_5$ complex fragments appear in the IR, which were assigned to the tungsten (2065 s [A₁], 1924 vs. cm⁻¹ [E]) and chromium part $(2052 \text{ s } [A_1], 1874 \text{ vs. cm}^{-1} [E])$ by comparison with $[W(CO)_5CNCH_2PPh_3]PF_6$ and literature data for $M(CO)_5/P-yl$ ide complexes [19]. Metal coordination of the ylidic carbon atom causes the v(CN) frequency to shoot up almost as high as the values of the protonated forms [CNCH₂PPh₃]PF₆ (2149 s cm⁻¹) and $[W(CO)_5CNCH_2PPh_3]PF_6$ (2161 s cm⁻¹), which lie ca. 90 cm⁻¹ or, respectively, 62 cm⁻¹, above those of the ylides CNCHPPh3 and W(CO)5CNCHPPh3. Contrary to occasional comments the presence or absence of a lone pair at the α atom obviously has quite a strong effect on the v(CN) frequency, a conclusion of particular relevance for the N-isocyanide chemistry [22]. A similar though completely expected course is taken by the chemical shift of the methin or, respectively, methylene proton in the ¹H NMR spectrum, viz. from 5.32 (d, ${}^{2}J_{PH} = 10$ Hz, [CNCH₂PPh₃]PF₆) to 2.99 (d, ${}^{2}J_{PH} =$ 28.5 Hz, CNCHPPh₃) to 5.25 (d, ${}^{2}J_{PH} = 8$ Hz, 1) (see Experimental Section) [23].



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2. Stabilization of Metallo Nitrile Ylides by Coordination to a Second Transition Metal

Early attempts to deprotonate the complexes $M(CO)_5CNCHPh_2$ (M = Cr, W) with stoichiometric amounts of LinBu or NaH in tetrahydrofuran at low temperatures (-78 °C) led to yellow salt-like solids, which were insoluble in organic media. The IR spectra of the partly pyrophoric products displayed marginally shifted but definitely weaker v(CN)bands ($\approx 2190 \text{ m cm}^{-1}$) and lower v(CO) frequencies indicative of anionic carbonyl complexes. The same reaction with KOtBu, on the other hand, gave a product whose IR spectrum showed no v(CN) absorption at all [24a]. More promising was the reaction of W(CO)5CNCH2SO2-p-tolyl with $Na[N(SiMe_3)_2]$ in toluene at -20 °C. The white precipitate turned out to be soluble in water and THF, showed the required IR spectroscopic data and even analyzed correctly (Experimental Section) [24a, 24b]. Still, what all these products have in common is their *non*-reversibility to the starting materials by protonation with aqueous HCl or HCl-gas in organic media. In view of these findings the assignment of the IR spectroscopic features between 2150 and 2200 cm⁻¹ to v(CN) vibrations appears questionable.

Note, however, that our studies of [3+2] cycloadditions with metallo nitrile vlides were carried out with solutions containing low stationary concentrations of the 1,3-dipoles. These solutions were prepared from $M(CO)_5CNCH_2R$ (M = Cr, W; $R = CO_2Me$, CO_2Et , SO_2 -*p*-tolyl) and stoichiometric amounts of LinBu, NaH or NEt₃ in THF at low temperatures showing no sign of decomposition (see below and literature [9b, 25]). As early as 1968, a first triphenylborio nitrile ylide – Li[Ph₃B– CNCPh₂] - similarly described as "shortly stable in solution" had been reported by Hesse and co-workers [26]. Also note that the action of Na[N(SiMe₃)₂] (or of other typical bases) on $M(CO)_5CNCH_2CO_2Et$ (M = Cr, W) came up with a cleavage of the ester group thereby opening a synthetic access to isocyanoacetato complexes [27]. A totally different course transformation of a cis-CO into a CN- ligand to give $Na[M(CN)(CO)_4CNCy]$ – is taken by the reaction between $Na[N(SiMe_3)_2]$ and $M(CO)_5CNCy$ (M = Cr, W) [24c].

Partial success was eventually achieved by treatment of a solution of Li[W(CO)5CNCHCO2Et] with MnBr(CO)5. Though available only in low yield and not analytically pure, the yellow crystalline product is formulated as compound 2 mainly on the basis of the mass spectrum, which shows the molecular peak followed by a series of lines arising from the successive loss of CO. In the IR spectrum, expectedly, the W(CO)₅CNCHCO₂Et part appears practically unchanged, whereas the v(CO) bands of the Mn(CO)₅ group partially experience a considerable shift to lower wavenumbers (Experimental Section). The reaction of the same tungstenio nitrile ylide with equimolar amounts of ReBr(CO)5 at -78 °C only brought gradual improvements: the structure of the yellow amorphous product **3** is confirmed by its IR, ¹H-NMR and, particularly, mass spectrum containing the full set of expected lines; still, varying analyses point to an easy decomposition of the compound. Further experiments with the chloro complexes





The first stable complex of the labile species "metallo nitrile vlide" 4 has been obtained from Li[W(CO)₅CNCHCO₂Et] and $Fe(Cl)Cp(CO)_2$ and structurally identified by the usual spectroscopic methods (Experimental Section). It forms orange crystals, which even melt without decomposition (!). Other stable complexes resulted from the reaction of stoichiometric amounts of pentacarbonyl(carbethoxymethylisocyanide)chromium and -tungsten with n-butyllithium and cis-dichlorobis(triethylphosphane)platinum. Simple recrystallization afforded colorless crystals of 5a and 5b, which analyzed correctly and turned out to be of sufficient quality for X-ray diffraction studies (cf. 3.). The IR spectra combine the characteristic band patterns of both complex components of which only the $v(CO_2)_{ester}$ absorptions show a remarkable downshift of 30 cm⁻¹ as compared with the parent isocyanide complexes indicating a residual carbanionic nature of the newly platinumbonded a-C-atom. More structure-relevant data are provided by NMR spectroscopy. Thus **5b** gives rise to two 31 P NMR signals at $\delta = -10.1$ (P1) and -6.6 (P2) with pairs of satellites indicating nonequivalent phosphorus atoms, i.e., a cis-Pt(PEt₃)₂ arrangement. Moreover, since the markedly different ¹J(¹⁹⁵Pt, ³¹P) coupling constants of 2231 (P1) and 3838 Hz



Figure 1. ORTEP plot and labelling scheme of complex **5b**. Ethyl hydrogen atoms are omitted for clarity and the thermal ellipsoids are drawn at the 30 % probability level. Selected bond lengths /Å and angles /°:W–C2 2.11(3), W–C3 1.96(3), (W–C0_{cis})_{av}. 2.015, C2–N 1.12(3), N–C1 1.43(4), C1–H1 0.96(6), C1–C8 1.48(3), C8–O2 1.22(3), C8–O1 1.31(3), O1–C9 1.46(3), Pt–C1 2.16(2), Pt–C1 2.363(6), Pt–P1 2.313(7), Pt–P2 2.248(5);W–C2–N 177(2), C2–N–C1 172(2), N–C1–C8 114(2), N–C1–Pt 109(1), C1–C8–O2 123(3), C1–C8–O1 113(2), O2–C8–O1 124(2), C1–Pt–C1 84.2(5), C1–Pt–P2 87.0(5), P1–Pt–P2 104.6(2), P1–Pt–C1 84.2(2).



(P2), respectively, are known to inversely reflect the different *trans*-influence Cl < 'C'-ligand, a 1:1 assignment δ -value/P atom is reached (Figure 1 and Experimental Section) [28]. The ¹H NMR spectra of **5a**,**b** are dominated by two broad multiplets between 1.0 and 2.5 ppm arising from the PEt₃ protons; the mainly interesting α -CH signals, though of exceedingly low intensity, correspond in all details with the postulated structure by showing the typical form of the X part of an ABX spin system, viz. two doublets of equal intensity plus platinum satellites. The two (P, H)-coupling constants agree perfectly with those found for $[Pt(Me)(NO_3)dppe]$ (dppe = 1,2-bis(diphenylphosphanyl)ethane) or $cis-[Pt(Cl)(CH_2CN)(PPh_3)_2]$, which served for comparison [29, 30]. Following these works the higher ${}^{3}J({}^{31}P, H)$ has been assigned to the coupling with the trans-P-ligand. The (¹⁹⁵Pt, H) coupling constant could only be determined for 5a; with a value of 87.2 Hz 5a unequivocally belongs to the class of cis-configured complexes of the type $PtX(Me)(PPh_3)_2$ (X = Cl, Br, N₃, NCS, NO₂). For the *trans*-isomers the ${}^{2}J({}^{195}\text{Pt}, \text{ H})$ amount to > 105 Hz, again a consequence of the weaker trans influence (trans effect) of X as against P, which strengthens the (¹⁹⁵Pt, H)-coupling [31].



Further platinum-stabilized chromio- and tungstenio nitrile vlides (6, 7) have been obtained in good yield by reaction of $M(CO)_5CNCH_2CO_2R$ (M = Cr, W; R = Et, Me) with the chloro-bridged dinuclear dication $[(Ph_3P)_2Pt(\mu-Cl)_2-$ Pt(PPh₃)₂](BF₄)₂ in the presence of LinBu. In their characteristic features the IR spectra of course are very similar to those of 5. An additional strong band at 550 cm^{-1} in the spectrum of 6 suggests cis-configuration of the bis(triphenylphosphane)platinum unit [32]. At first glance this seems inconsistent with the ³¹P-NMR spectrum showing only one singlet though with two sets of platinum satellites. Obviously an accidental coincidence of the non-equivalent cis-positioned phosphorus nuclei has to be assumed. The most interesting ¹H-NMR signal, that of the α -CH proton, is partly hidden under the quartet of the ester group; mainly for this reason we

also synthesized **7a,b**. Unfortunately, this time the α -CH proton signal coincided with that for methyl and THF, which was contained in the crystal (Experimental Section).

With the synthesis of **8** from *trans*-[Pt(Cl)(CNCH₂CO₂Et)-(PPh₃)₂]BF₄, KOtBu and [(Ph₃P)₂Pt(μ -Cl)₂Pt(PPh₃)₂](BF₄)₂ a first platinio nitrile ylide could be stabilized by coordination to platinum. The salt-like stable product, which crystallizes in large rods can also be described as an α -deprotonated carbethoxymethyl isocyanide C,C'-bridging two platinum complex fragments. Its low solubility did not allow to obtain instructive NMR spectra; in the IR ν (CO₂Et) as well as ν (CN) appear somewhat shifted to lower wavenumbers.

Benzylisocyanide complexes had proven unreactive as regards [3+2] cycloadditions. So it was surprising that $Cr(CO)_5CNCH_2Ph$ reacted with [(Ph₃P)₂Pt(μ -Cl)₂Pt(PPh₃)₂]-(BF₄)₂ in the presence of a mixture of LinBu and NaH (1:1) to give a powdery product, which according to the IR spectrum contained both complex reactants suggesting *a*-platination had taken place. The elemental analysis of the colorless fraction, which was obtained after repeated recrystallization however points to a doubly platinated product **9**, which needs further investigation. In this context *van Leusen*'s claim of *a*-dilithiated tosylmethylisocyanide – CN–CLi₂–SO₂–*p*-tolyl – as an isolable intermediate as well as our "permetallated methylisocyanide" (OC)₅Cr–C≡N–C≡[Co₃(CO)₉] deserves mentioning [33, 34].



Above we could demonstrate that metallo nitrile ylides, or, which is the same, α -deprotonated isocyanide complexes coordinate to transition metals through the trivalent carbon representing the negative end of the 1,3-dipole or, respectively, the α -carbanion. In most cases the gain in stability was sufficient to allow the dinuclear products to be isolated and stored over prolonged periods. This kind of fixation of labile intermediates might well play a decisive role in catalytic processes. An example is the Cu₂O-catalyzed cycloaddition of unsaturated esters and nitriles to α -CH–acidic isocyanides, which *Saegusa* postulated to proceed via complex **G** [35]. Extensions to include 1,3-dipoles seem appropriate. We have not investigated the availability of the *stabilized* metallo nitrile ylides for [3+2] cycloadditions, however.



3. X-ray Structure of 5b

The crystal lattice of **5b** is made up of discrete molecules with the expected primary structure, which combines that of a functionalized (α -metallated) methylisocyanide coordinated to W(CO)₅ with that of a chlorobis(triethylphosphane)platinum(II) complex carrying a functionalized methyl ligand (Figure 1). Special areas of interest are

- The stereochemistry of the coordination sphere of tungsten whose W–CO bonds of varying length – $d(W-C(O)_{ax})$ [1.96(3) Å] is markedly shorter than the average bond between W and the equatorial CO ligands $[d(W-C(O)_{eq})_{av}] =$ 2.02(2) Å] – reflect the donor capacities of a typical C-isocyanide. At the same time this ligand gives rise to the longest tungsten to carbon bond in **5b** [d(W-C2) = 2.11(3) Å] and a practically linear W–C2–N arrangement [177(2)°], totally in line with the accumulated data on other carbonyl/isocyanide tungsten complexes [36].

- The stereochemistry about platinum, which is planar - the X–Pt–Y angles add up to exactly 360.0° – but not at all square: the P1-Pt-P2 angle $[104.6(2)^{\circ}]$ formed by the *cis*-Pt(PEt₃)₂ group is almost 20° larger than the average of the other three (85.1°), and the platinum to P2 bond *trans* to Cl [2.248(5) Å] is considerably shorter than Pt-P1 [2.313(7) Å] trans to the functionalized methyl ligand though both values still correspond with the order of Pt-P bond lengths generally found in (phosphane)platinum(II) complexes [37-40]. Since ¹J(¹⁹⁵Pt, ³¹P)-coupling constants logically decrease with increasing Pt-P bond lengths and vice versa our assignment of the smaller ${}^{1}J(Pt,P)$ value to P1 reached above thus is confirmed. The Pt–Cl bond length [2.363(6) Å] is in the normal range [41, 42], whereas the platinum to carbon bond [2.16(2) Å] is markedly longer than calculated from the covalent radii (2.08 Å) and also longer than the Pt-C bonds in trans-[Pt(Cl)(R)(phosphane)₂] {R = CH₂CN, phosphane = $PPh_3: d(Pt-C) = 2.08(1) \text{ Å} [43]; R = Me, phosphane =$ PMePh₂: d(Pt-C) = 2.081(6) Å [44]}. The Pt-C bond length in trans-Pt(CH₂CN)(H)(PPh₃)₂ of 2.16(1) Å, on the other hand, seems to suggest comparable trans-influences for the PEt₃ and hydrido ligands [45] (Figure 1).

- The ascertained arrangement of a (coordinated) metallo nitrile ylide in comparison with the one calculated for the (free) organic analogue [46]. Whereas both C–N–C skeletons are slightly bent at the nitrogen atom, a fundamental difference between these 1,3-dipoles exists in their reversed polarities, i.e., the carbanionic center, which resides at the divalent carbon atom C1 in organic systems passes on to the trivalent carbon atom C2 in metallo derivatives (**H**, **I**). Under the influence of the electron-rich metal (W^0), which stabilizes carbonium spe-



cies, the allenyl anion-type resonance formula **H** with two C= N double bonds already loses most of its significance in favor of the more asymmetric propargyl (here: classical isocyanide complex) form **I**; coordination to a second metal (Pt^{II}) through C2 then causes a further shortening of the C1–N and lengthening of the N–C2 bond to end up with the established *C*-isocyanide complex structure.



4. Stabilization of Metallo Nitrile Imines by Coordination to a Second Transition Metal

Preparation and stabilization of the second type organometallic analogue of *Huisgen*'s "organic" 1,3-dipoles, the chromio nitrile imine $[(OC)_5CrC\equiv N^+-N^-H]^-$, closely followed the method established for metallo nitrile ylides [47]. Deprotonation of the parent pentacarbonyl(isodiazomethane)chromium occurred with triethylamine in fourfold excess to generate a low concentration of the 1,3-dipole, which was immediately treated with the Lewis-acidic metal complexes FeCp(Cl)(CO)₂ and $[Pt(\mu-Cl)(PPh_3)_2]_2(BF_4)_2$ to give the moderately stable products **10** and **11** the latter of which is reasonably well characterized by IR and ¹H NMR spectroscopy and elemental analysis (Experimental Section).



Conclusion

 α -Deprotonated C- and N-isocyanide complexes represent true organometallic analogues of Huisgen's "organic" 1,3-dipoles, nitrile ylides, and nitrile imines, respectively, as is clearly evident from their [3+2]-cycloaddition chemistry [8-10]. With the exception of $M(CO)_5CNCHPPh_3$ (M = Cr, W), which are stable substances due to the presence of the carbanion-stabilizing phosphonio substituent, all other studied metallo nitrile ylides and metallo nitrile imines only exist as shortlived intermediates generated and reacted "in situ". "Stabilization by coordination" to an appropriate second transition metal now proved to be the method of choice to get hold of these interesting species. Best results were achieved with cationic platinum complex fragments in accord with the well-known ability of this metal to form particularly stable metal-carbon bonds. The most striking consequence of the fixation of the chromio and tungstenio nitrile ylides as ligands in platinum(II) [and iron(II)] complexes perhaps is that the products 4-7 even melt without decomposition.

Experimental Section

General Remarks: All experiments were performed under argon in dried argon-saturated solvents. $[W(CO)_5CNCH_2PPh_3]PF_6$ [12], $W(CO)_5CNCH_2SO_2$ -*p*-tolyl [9b], $Cr(CO)_5CNCH_2Ph$ [9b], $Cr(CO)_5CNCH_2CO_2Et$ [25], $W(CO)_5CNCH_2CO_2Et$ [25], $Cr(CO)_5CNNH_2$ [13, 48], $[Re(CO)_6]PF_6$ [49], $[FeCp(CO)_2CS]PF_6$ [50, 51], $[FeCp(CO)(CNPh)_2]PF_6$ [51], and $[FeCp(CNPh)_3]Cl$ [51, 52] were prepared according to literature procedures.

IR spectra were recorded with a Zeiss IMR 16 and IRM 25, Perkin– Elmer Mod. 621, and Beckman IR 12 spectrometers, NMR spectra with a Jeol JNM-PMX-60 or a Jeol JNM-PS-100. Mass spectra were recorded with a Varian CH-5 (excitation energy 70 eV). Microanalyses (C, H, N) were obtained with a Heraeus CHN Rapid-Elementanalysator. Melting or decomposition points were determined with a Büchi Modell 510 melting point apparatus and are uncorrected.

Syntheses

 μ -{Isocyanomethylenetriphenylphosphorane-C,C'}pentacarbonyltungsten-pentacarbonylchromium (1): A solution of Cr(CO)₅THF prepared by photolysis of hexacarbonylchromium (0.70 g, 3.18 mmol) in tetrahydrofuran (200 mL) as described in the literature [53] was reduced to about half its volume and combined with a solution of W(CO)₅CNCHPPh₃ prepared from [W(CO)₅CNCH₂PPh₃]PF₆ (2.14 g, 2.5 mmol) and NaNH₂ (3.0 g, 75 mmol) in toluene (150 mL) according to a procedure published earlier [9d]. After stirring for 4 h at 0 °C the solvent, excess Cr(CO)₆, and possibly formed W(CO)₅CNMe were removed in high vacuum at 25-30 °C. The residue was dissolved in CH₂Cl₂ (ca. 20 mL) and the solution was filtered and layered with two times the volume of petroleum ether. At -15 °C compound 1 separated as yellow microcrystals (m.p. 138 °C, dec.), which were slightly soluble in ethyl ether and soluble in polar solvents such as CH2Cl2 or acetone. There, however, slow decomposition took place. Yield 0.84 g (41 % rel. to [W(CO)₅CNCH₂PPh₃]PF₆). C₃₀H₁₆CrNO₁₀PW (817.28): calcd. C 44.09, H 1.97, N 1.71 %; found C 43.54, H 2.20, N 2.48 %. **IR** (KBr): $\tilde{v} = 2143$ s [v(CN)]; 2065 s, 2052 s, 1924 vs, 1874 vs. $[v(CO)] \text{ cm}^{-1}$. **IR** (CH₂Cl₂): $\tilde{v} = 2062 \text{ s}, 2050 \text{ s} [v(CO)-A_1] \text{ cm}^{-1}$. ¹**H NMR** (60 MHz, CD₃CN): δ = 7.8 (m, CH_{arom}, 15 H); 5.25 (d, J_{PH} = 8 Hz, 1 H). ³¹**P** NMR (90 MHz, CH₂Cl₂): δ = 31.7 ppm.

Attempted Isolation of the 1,3-Dipole Na[W(CNCHSO₂-*p*-tolyl)(CO)₅]: A solution of Na[N(SiMe₃)₂] (0.17 g, 0.93 mmol) in toluene (30 mL) was filtered through sea sand, cooled to -30 °C and added to a solution of W(CO)₅CNCH₂SO₂-*p*-tolyl (0.48 g, 0.93 mmol) in toluene (50 mL). After 40 min the colorless precipitate was filtered off through a cooled frit (-20 °C), washed thoroughly with cold toluene and petroleum ether and dried in high vacuum. On warming to room temperature no changes could be observed. The substance was easily soluble in THF and water; in the latter it soon came to clouding, however. Yield 0.375 g (75 %). C₁₄H₈NaNO₇SW (541.12): calcd. C 31.07, H 1.49, N 2.59 %; found C 30.36, H 1.87, N 2.56 %.

(OC)₅**W**{*u*-CNCH(CO₂Et)}**Mn(CO)**₅ **(2):** A solution of W(CO)₅CNCH₂CO₂Et (0.775 g, 1.77 mmol) in THF (70 mL) was dried with Li[AlH₄] and cooled to -78 °C. After addition of Li*n*Bu (1.2 mL of a 1.6 M solution in *n*-hexane) stirring was continued for 30 min. during which a colorless product precipitated. Afterwards, a solution of MnBr(CO)₅ (0.487 g, 1.77 mmol) in THF (50 mL), also cooled to -78 °C, was added dropwise, and the mixture was stirred for another 2 h at low temperature. It was allowed to gradually warm to room temperature, then the solvent was removed and the residue dis-

solved in benzene. The solution was filtered, and the product was precipitated with petroleum ether. Repeated recrystallization from dichloromethane/*n*-pentane and benzene/*n*-pentane gave a yellow microcrystalline compound in low yield. **IR** (CHCl₃): $\tilde{v} = 2179$ m [v(CN)]; 2069 m, 2045 m, 2012 s, 1950 vs. [v(CO)]; 1750 m [$v_{as}(CO_2)_{ester}$] cm⁻¹. For comparison, **IR** [W(CO)₅CNCH₂CO₂Et/ CHCl₃]: $\tilde{v} = 2178$ m [v(CN)]; 2065 m, 1975 sh, 1948 vs. [v(CO)] cm⁻¹. **IR** [MnBr(CO)₅/ CCl₄]: $\tilde{v} = 2133$ w, 2050 s, 2019 w, 2001 m [v(CO)] cm⁻¹ [54].

(OC)₅W{*µ*-CNCH(CO₂Et)}Re(CO)₅ (3): А solution of W(CO)₅CNCH₂CO₂Et (0.31 g, 0.71 mmol) in THF (30 mL) was cooled to -78 °C. To this an equimolar amount of LinBu (15 % solution in *n*-hexane) was added dropwise. After 30 min the reaction was complete. Afterwards, ReBr(CO)₅ (0.29 g, 0.7 mmol) was added, and the mixture was allowed to warm to room temperature. The solvents were removed, and the residue was extracted with 3×20 mL of ethyl ether. By addition of *n*-hexane compound 3 could be precipitated from the orange ethereal solution as yellow powder. Yield 0.36 g (67 %). **IR** (KBr): $\tilde{v} = 2180$ w [v(CN)]; 2102 w, 2082 m, 2048 s, 1920 vs. [v(CO)]; 1718 m $[v_{as}(CO_2)_{ester}]$ cm⁻¹. ¹H NMR (60 MHz, CDCl₃): $\delta =$ 4.47 + 4.36 (s, CH + q, CH₂, 3 H), 1.44 (t, Me, ${}^{3}J_{HH} = 7.2$ Hz, 3 H). **MS** (EI, 70 eV, 130 °C): m/z = 762 (32) [M]⁺; 734 (5), 706 (26), 678 (21), 650 (36), 622 (38), 594 (68), 566 (56), 538 (65), 510 (31), 482 (24) $[M - n(CO)]^+$ (n = 1–10); 438 (100) $[M - W(CO)_5]^+$; 436 $[M - W(CO)_5]^+$; 438 $[M - W(CO)_5]^+$; 436 $[M - W(CO)_5]^+$; 436 $[M - W(CO)_5]^+$; 438 $\operatorname{Re(CO)_5}^+$

 $(OC)_5W{\mu-CNCH(CO_2Et)}FeCp(CO)_2$ (4): At -78 °C a solution containing Li[W(CNCHCO₂Et)(CO)₅] (0.71 mmol) (see preceding procedure) reacted with FeCp(Cl)(CO)₂ (0.15 g, 0.70 mmol), afterwards the mixture was allowed to warm to room temperature. Removal of the solvent left a red residue, which was extracted with ethyl ether $(3 \times 20 \text{ mL})$. The combined orange-red ether extracts were again taken to dryness, and the resulting material was recrystallized from CH₂Cl₂/ *n*-hexane (1:1) at -25 °C to give orange crystals of 4, m.p. 72 °C. Yield 0.13 g (31 %). On further addition of *n*-hexane deep red [FeCp(CO)₂]₂ separated. C₁₇H₁₁FeNO₉W (612.98): calcd. C 33.31, H 1.81, N 2.29 %; found C 33.39, H 1.81, N 2.32 %. **IR** (KBr): $\tilde{v} = 2173$ m [v(CN)]; 2075 s, 2032 s, 1989 s, 1980 s, 1920 vs. [v(CO)]; 1713 m $[v_{as}(CO_2)_{ester}]$ cm⁻¹. **IR** (CH₂Cl₂): $\tilde{v} = 2165$ m [v(CN)]; 2078 s, 2042 s, 1990 s, 1940 vs. [v(CO)]; 1715 m $[v_{as}(CO_2)_{ester}]$ cm⁻¹. ¹H NMR (60 MHz, CDCl₃): δ = 4.90 (s, Cp, 5 H), 4.24 + 4.19 (s, CH + q, CH₂, 3 H), 1.32 (t, Me, ${}^{3}J_{\text{HH}} = 7.0$ Hz, 3 H). **MS** (EI, 70 eV, 150 °C): m/z = 613 (89) [M]⁺; 585 (2), 557 (38), 529 (18), 501 (42), 473 (100), 445 (91), 417 (94) $[M - n(CO)]^+$ (n = 1-7); 540 (4) $[M - CO_2Et]^+$.

 $(OC)_5Cr{\mu-CNCH(CO_2Et)}Pt(Cl)(PEt_3)_2$ (5a): A solution of Cr(CO)₅CNCH₂CO₂Et (1.470 g, 4.80 mmol) in THF (5 mL) was cooled to -65 °C. To this LinBu (310 mg, 4.80 mmol) (15 % solution in n-hexane) was added dropwise. After 5 min a suspension of cis-PtCl₂(PEt₃)₂ (2.42 g, 4.80 mmol) in THF (20 mL) was added whilst stirring. Stirring was continued for 4 h, during this time the mixture was allowed to warm to room temperature. A cloudy solution had formed, which was filtered and the solvents were evaporated to dryness. Through grinding in petroleum ether (40 mL) the resulting yellow-brown oil could be brought to crystallize. The off-white powder was dissolved in 25 mL of CHCl₃, the solution filtered and concentrated to about 5 mL. Layering with petroleum ether caused large colorless parallelepipeds (m.p. 118 °C) to grow within 10 h. Extensive washing of the crystals with petroleum ether or repeated recrystallization should be avoided as this led to gradual decomposition. Yield 3.06 g (83 %). C₂₂H₃₆NO₇ClCrP₂Pt (771.03): calcd. C 34.27, H 4.71, N 1.82 %; found C 34.59, H 4.70, N 1.81 %. **IR** (KBr): $\tilde{v} = 2180$ s [v(CN)]; 2068 s, 1988 s, 1945 vs, 1908 vs. [v(CO)]; 1729 sh, 1722 s

 $[v_{as}(CO_2)_{ester}]$; 1188 s $[v_s(CO_2)_{ester}]$ cm⁻¹. **IR** (CH₂Cl₂): $\tilde{v} = 2180$ s [v(CN)]; 2060 s, 1985 sh, 1940 vs. [v(CO)]; 1720 s $[v_{as}(CO_2)_{ester}]$; 1195 s $[v_s(CO_2)_{ester}]$ cm⁻¹. ³¹P{¹H} **NMR** (60 MHz, CD₂Cl₂): $\delta = -10.1$ (s + sat., P1, ¹J_{PtP1} = 2231 Hz), -6.6 (s + sat., P2, ¹J_{PtP2} = 3838 Hz). ¹H **NMR** (60 MHz, CDCl₃): $\delta = 4.69$ (dd + sat., CNCH, ³J_{P1H} = 10.2 Hz; ³J_{P2H} = 6.4 Hz; ²J_{PtH} = 87.2 Hz, 1 H), 4.24 (q, CH₂-ester, ³J_{HH} = 7.0 Hz, 2 H), 2.5–1.7 (m, CH₂-phosphane, 12 H), 1.7–1.0 (m, CH₃-phosphane + CH₃-ester, 21 H).

(OC)₅W{ μ -CNCH(CO₂Et)}Pt(Cl)(PEt₃)₂ (5b): The complex was prepared from W(CO)₅CNCH₂CO₂Et (900 mg, 2.06 mmol), Li*n*Bu (132 mg, 2.06 mmol) (15 % solution in *n*-hexane), and *cis*-PtCl₂(PEt₃)₂ (1.035 g, 2.06 mmol) as described for 5a. Yield 1.36 g (73 %), m.p. 127 °C. C₂₂H₃₆NO₇ClP₂PtW (902.88): calcd. C 29.27, H 4.02, N 1.55 %; found C 29.38, H 4.27, N 1.50 %. **IR** (KBr): $\tilde{v} = 2180$ s [v(CN)]; 2063 s, 1989 s, 1930 vs,b, 1900 vs. [v(CO)]; 1726 sh, 1721 s [v_{as}(CO₂)_{ester}]; 1185 s [v_s(CO₂)_{ester}] cm⁻¹. **IR** (CH₂Cl₂): $\tilde{v} = 2180$ s [v(CN)]; 2060 s, 1990 sh, 1940 vs. [v(CO)]; 1720 s [v_{as}(CO₂)_{ester}]; 1190 s [v_s(CO₂)_{ester}] cm⁻¹. ¹**H NMR** (60 MHz, CDCl₃): $\delta = 4.61$ (dd + sat., CNCH, ³J_{P1H} = 10.8 Hz; ³J_{P2H} = 6.4 Hz; ²J_{PtH} = not obsvd., 1 H), 4.17 (q, CH₂-ester, ³J_{HH} = 7.0 Hz, 2 H), 2.6–1.7 (m, CH₂-phosphane, 12 H), 1.7–0.9 (m, CH₃-phosphane + CH₃-ester, 21 H).

(OC)₅Cr{µ-CNCH(CO₂Et)}Pt(Cl)(PPh₃)₂ (6): A solution of Cr(CO)₅CNCH₂CO₂Et (591 mg, 1.94 mmol) in THF (30 mL) was cooled to -65 °C. To this LinBu (124 mg, 1.94 mmol) (15 % solution in n-hexane) and a suspension of [PtCl(PPh₃)₂]₂(BF₄)₂ (1.632 g, 0.97 mmol) in THF (10 mL) were added. Stirring was continued for 5 h during which the mixture was allowed to warm to room temperature. By now a dark yellow solution had formed and a colorless solid was suspended, which was collected on a frit and recrystallized from THF/petroleum ether to give a mixture of needle- and cube-shaped colorless crystals. A further crop of crystals could be obtained by lavering the filtrate with petroleum ether. Overall yield 1.87 g (91 %). The compound began to melt at 144 °C, but solidified again forming yellow needles at ≈ 163 °C; at 193 % it decomposed leaving a clear red melt. C₄₆H₃₆NO₇ClCrP₂Pt [calcd. 1058.90; found (osmom. in CH₂Cl₂) 1068]: calcd. C 52.18, H 3.43, N 1.32, Cl 3.35 %; found C 51.80, H 3.67, N 1.07, Cl 3.27 %. **IR** (KBr): $\tilde{v} = 2175$ s [v(CN)]; 2063 s, 1988 s, 1955 sh, 1932 vs. [v(CO)]; 1733 s [vas(CO₂)ester]; 1202 s, 1190 sh $[v_{s}(CO_{2})_{ester}]$, 550 s $[v(cis-Pt(PPh_{3})_{2}]$ cm⁻¹. IR $(CH_{2}Cl_{2})$: $\tilde{v} = 2175$ s [v(CN)]; 2065 s, 1995 sh, 1932 vs. [v(CO)]; 1732 s $[v_{as}(CO_2)_{ester}]$; 1190 s $[v_s(CO_2)_{ester}]$ cm⁻¹. ¹H NMR (60 MHz, CDCl₃): $\delta = 7.8-6.9$ (m, Ph, 30 H), 4.0-3.7 (m, CNCH + CO₂CH₂Me, 3 H), 4.26 (q, $CO_2CH_2Me + CNCH$, 3 H), 1.44 (t, $CO_2CH_2CH_3$, ${}^{3}J_{HH} = 7.0$ Hz, 3 H).

(OC)₅Cr{ μ -CNCH(CO₂Me)}Pt(Cl)(PPh₃)₂ (7a): The complex was prepared from Cr(CO)₅CNCH₂CO₂Me (500 mg, 1.72 mmol) (synthesized in total analogy with Cr(CO)₅CNCH₂CO₂Et [21]), LinBu (110 mg, 1.72 mmol), and [PtCl(PPh₃)₂]₂(BF₄)₂ (1.446 g, 0.86 mmol) as described for **6**. The colorless compound [Yield 1.02 g (0.91 mmol, 53 %), m.p.: 158 °C] crystallized with one molecule of THF. C₄₅H₃₄NO₇ClCrP₂Pt + 1THF (1117.38): calcd. C 52.67, H 3.79, N 1.25 %; found C 52.36, H 3.84, N 0.93 %. **IR** (KBr): $\tilde{\nu}$ = 2180 s [ν (CN)]; 2070 s, 1990 m, 1932 vs. [ν (CO)]; 1738 s [ν_{as} (CO₂)_{ester}]; 1205 m, 1185 sh [ν_{s} (CO₂)_{ester}] cm⁻¹. **IR** (CH₂Cl₂): $\tilde{\nu}$ = 2180 s [ν (CN)]; 2060 s, 1990 sh, 1945 vs. [ν (CO)]; 1745 s [ν_{as} (CO₂)_{ester}]; 1190 m [ν_{s} (CO₂)_{ester}] cm⁻¹. ¹H **NMR** (60 MHz, CDCl₃): δ = 7.7–7.1 (m, Ph, 30 H), 3.9–3.6 (m, CNCH + CO₂CH₃ + C₄H₈O, 12 H).

 $(OC)_5W{\mu-CNCH(CO_2Me)}Pt(Cl)(PPh_3)_2$ (7b): The complex was prepared from $W(CO)_5CNCH_2CO_2Me$ (100 mg, 0.24 mmol) (synthesized in total analogy with $W(CO)_5CNCH_2CO_2Et$ [21]), LinBu



(15 mg, 0.24 mmol) and [PtCl(PPh₃)₂]₂(BF₄)₂ (199 mg, 0.12 mmol) as described for **6**. Yield 0.18 g (0.15 mmol, 62 %). M.p.: 176 °C. C₄₅H₃₄NO₇ClP₂PtW (1177.12): calcd. C 45.92, H 2.91, N 1.19 %; found C 43.90, H 3.16, N 1.19 %. **IR** (KBr): $\tilde{v} = 2180$ s [v(CN)]; 2070 s, 1982 s, 1930 vs, b [v(CO)]; 1738 s [v_{as}(CO₂)_{ester}]; 1205 s, 1185 sh [v_s(CO₂)_{ester}] cm⁻¹. **IR** (CH₂Cl₂): $\tilde{v} = 2180$ s [v(CN)]; 2065 s, 1980 sh, 1940 vs. [v(CO)]; 1743 s [v_{as}(CO₂)_{ester}]; 1190 m [v_s(CO₂)_{ester}] cm⁻¹.

[(PPh₃)₂(Cl)Pt{µ-CNCH(CO₂Me)}Pt(Cl)(PPh₃)₂]BF₄ (8): [Pt(Cl)(CNCH₂CO₂Et)(PPh₃)₂]BF₄ (250 mg, 0.26 mmol), KOtBu (30 mg, 0.26 mmol), and [(Ph₃P)₂Pt(µ-Cl)₂Pt(PPh₃)₂](BF₄)₂ (219 mg, 0.13 mmol) were suspended in dichloromethane (40 mL) and stirred for 2 h at room temperature. The solvent was removed and the colorless powdery residue was stirred in ethyl ether (60 mL) for 12 h. The product was collected on a frit, dried at 40 °C in high vacuum and recrystallized from CH2Cl2/ether to give 0.31 (0.18 mmol, 69 %) of rod-shaped (dec.)]. colorless crystals [m.p.: 294 °C C₇₇H₆₆NO₂BCl₂F₄P₄Pt₂ (1709.18): calcd. C 54.11, H 3.89, N 0.82 %; found C 54.14, H 4.31, N 0.82 %. **IR** (KBr): $\tilde{v} = 2230$ m [v(CN)]; 1720 m, b $[v_{as}(CO_2)_{ester}]$; 1195 s $[v_s(CO_2)_{ester}]$; 1060 vs, b $[v(BF_4)]$ cm⁻¹. IR (CH₂Cl₂): $\tilde{v} = 2225 \text{ s} [v(CN)]$; 1720 s, 1710 m [$v_{as}(CO_2)_{ester}$]; 1202 m $[v_{s}(CO_{2})_{ester}]$; 1055 vs. $[v(BF_{4})]$ cm⁻¹.

 $(OC)_5Cr{\mu_3-CNCPh}[Pt(Cl)(PPh_3)_2]_2$ (9): Cr(CO)5CNCH2Ph (309 mg, 1.0 mmol) and [(Ph₃P)₂Pt(µ-Cl)₂Pt(PPh₃)₂](BF₄)₂ (1.684 g, 1.0 mmol) were dissolved in THF (20 mL). To this sodium hydride (24 mg, 1.0 mmol) (from a 50 % suspension in paraffin) was added at -78 °C and the mixture was allowed to warm to -40 °C during 2 h. A solution of *n*-butyllithium (64 mg, 1.0 mmol) in THF (10 mL) was added dropwise at first resulting in an intensive orange coloring, which turned to bright green after a while. Warming up to room temperature led to a red solution, which was filtered through cellulose (0.5 \times 5 cmcolumn), concentrated to about 1/5 of the original volume and layered with a small amount of petroleum ether. On standing at 6 °C for a couple of hours a microcrystalline powder separated. Repeated recrystallization from THF/petroleum ether resulted in diamond-shaped colorless single crystals. Yield 0.20 g (0.11 mmol, 11 %). M.p.: 286 °C (dec.). C₈₅H₆₅NO₅Cl₂CrP₄Pt₂ (1817.46): calcd. C 56.17, H 3.60, N 0.77 %; found C 56.33, H 3.81, N 0.69 %. IR (KBr): $\tilde{v} = 2160$ s [v(CN)]; 2055 s, 1990 m, 1950 sh, 1927 vs, b [v(CO)] cm⁻¹. IR (CH_2Cl_2) : $\tilde{v} = 2160 \text{ s} [v(CN)]$; 2055 s, 1985 sh, 1940 vs. $[v(CO)] \text{ cm}^{-1}$.

(OC)₅Cr{µ-CNN(H)}FeCp(CO)₂ (10): (a) Preparation of NEt₃H[Cr{CNNH}(CO)₅]: A solution of Cr(CO)₅CNNH₂ (0.24 g, 1.0 mmol) in THF (40 mL) was cooled in an ice bath. To it a fourfold molar amount of NEt3 was added, and the mixture war stirred for 15 min after which it could be employed in further reactions. (b) Reaction with FeCl(Cp)(CO)₂: The nitrile imine solution (see above) was cooled to -78 °C. FeCl(Cp)(CO)2 (0.21 g, 1.0 mmol) was added, and the mixture was allowed to warm to room temperature overnight. The red to orange solution was taken to dryness, and the residue was extracted with three 20 mL portions of ethyl ether. Removal of the solvent from the combined extracts followed by recrystallization of the crude product gave 0.13 g (32 %) of 10 as an ochre powder. IR (KBr): $\tilde{v} = 3380 \text{ vw} [v(\text{NH})]; 2212 \text{ m} [v(\text{CN})]; 2125 \text{ m}, 2060 \text{ s}, 1985 \text{ sh}, 1918$ vs. [v(CO)] cm⁻¹.

(OC)₅Cr{ μ -CNN(H)}Pt(Cl)(PPh₃)₂ (11): NEt₃H[Cr{CNNH}(CO)₅] (0.5 mmol) reacted with [PtCl(PPh₃)₂]₂(BF₄)₂ (0.42 g, 0.25 mmol) as described for 10. An analogous work-up procedure gave 0.3 g (61 %) of 11 as a pale yellow powder. C₄₂H₃₁ClCrN₂O₅P₂Pt (988.34): calcd. C 51.05, H 3.16, N 2.83 %; found C 51.57, H 3.75, N 3.06 %. **IR** (KBr): $\tilde{\nu} = 3420$ w [ν (NH)]; 2235 w [ν (CN)]; 2060 m, 1980 m, 1926

vs. [ν (CO)] cm⁻¹. ¹**H NMR** (60 MHz, CDCl₃, 40 °C): δ = 8.22 (broad s, NH, 1 H), 7.20 (m, Ph, 30 H).

X-ray Structure of 5b: Single crystals suitable for X-ray diffraction studies were grown from a concentrated THF solution of 5b layered with petroleum ether. Crystallographic data were collected with a PHILIPS PW 1100 four circle-diffractometer at 20 °C in the ω -2 θ scan mode using Ag- K_{a} -radiation ($\lambda = 0.5583$ Å) and a graphite-monochromator. Neither absorption nor extinction corrections were carried out. The phase problem was solved by applying the heavy atom approach, and the structure developed using alternative cycles of full-matrix least-squares refinement and difference-Fourier synthesis. Though at this stage most of the hydrogen positions could be made out, only that of H1 (located at the asymmetric carbon atom C1) was included in the list of atoms to be refined. All ethyl hydrogen coordinates were calculated and the C₂H₅ groups subsequently treated as "rigid bodies". The calculations were carried out using the program system SHELX-76 [55] with scattering factors for neutral atoms taken from the literature [56]. The molecular plot was produced with the ORTEP program [57].

C₂₂H₃₆ClNO₇P₂PtW (902.9), monoclinic, *P*2₁/*c* (Nr. 14), *a* = 14.077(4), *b* = 9.353(3), *c* = 24.127(6) Å, β = 97.75(2)°, *V* = 3147.6 Å³, *Z* = 4, ρ_{obsd} = 1.89(2), ρ_{calcd} = 1.905 Mg·m⁻³, temperature = 293 K, 2θ range for data collection = 3.0–22.0°, reflections collected = 8523, independent reflections = 4273, *R*_{int} = 0.0324 %, observed reflections = 2953 [*I* ≥ 2σ (*I*)], parameters (refined) = 292, *F*(000) = 1720, *R* = 5.97 %.

Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ. Copies of the data can be obtained on quoting the depository numbers CCDC-757433 (**5b**). (www.ccdc.cam.ac.uk/data_request/cif; Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk).

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References

- Metal Complexes of Functional Isocyanides, Part 32. Part 31: F. Schoder, U. Plaia, R. Metzner, W. Sperber, W. Beck, W. P. Fehlhammer, Z. Anorg. Allg. Chem. 2010, DOI: 10.1002/ zaac.200900456.
- [2] N. H. Toubro, A. Holm, J. Am. Chem. Soc. 1980, 102, 2093; H.-J. Hansen, H. Heimgartner, Nitrile Ylides, p. 177, P. Caramella, P. Grünanger, Nitrile Oxides and Imines, p. 291, in 1,3-Dipolar Cycloaddition Chemistry (Ed.: A. Padwa) vol. 1, Wiley, New York, 1984; J. T. Sharp, Nitrile Ylides and Nitrile Imines in The Chemistry of Heterocyclic Compounds, Vol. 59: Synthetic Applications of 1,3-Dipolar Cycloaddition Chemistry Toward Heterocycles and Natural Products (Eds.: A. Padwa, W. H. Pearson) Wiley, New York, 2002.
- [3] a) R. Huisgen, Angew. Chem. 1963, 75, 604; Angew. Chem. Int. Ed. Engl. 1963, 2, 565; b) R. Huisgen, Angew. Chem. 1963, 75, 742; Angew. Chem. Int. Ed. Engl. 1963, 2, 633; c) R. Huisgen, J. Org. Chem. 1976, 41, 403; d) R. Huisgen, 1,3-Dipolar Cycloadditions – Introduction, Survey, Mechanism, p. 1 in 1,3-Dipolar Cycloaddition Chemistry (Ed.: A. Padwa) vol. 1, Wiley, New York, 1984; e) R. Huisgen, The Adventure Playground of Mechanisms and Novel Reactions, ACS, Washington DC, 1994.

ARTICLE

- [4] a) E. P. Janulis Jr, S. R. Wilson, A. J. Arduengo III, *Tetrahedron Lett.* 1984, 25, 405; b) C. Wentrup, S. Fischer, H. M. Bestermann, M. Kuzaj, H. Lüerssen, K. Burger, *Angew. Chem.* 1986, 98, 99; *Angew. Chem. Int. Ed. Engl.* 1986, 25, 85.
- [5] a) G. Sicard, A. Baceiredo, G. Bertrand, J. Am. Chem. Soc. 1988, 110, 2663; b) G. Bertrand, C. Wentrup, Angew. Chem. 1994, 106, 549; Angew. Chem. Int. Ed. Engl. 1994, 33, 527.
- [6] a) N. Goldberg, M. Iraqi, H. Schwarz, *Chem. Ber.* 1993, *126*, 2353; b) G. Maier, C. Schmid, H. P. Reisenauer, E. Endlein, D. Becker, J. Eckwert, B. A. Hess Jr, L. J. Schaad, *Chem. Ber.* 1993, *126*, 2337.
- [7] N. Goldberg, A. Fiedler, H. Schwarz, *Helv. Chim. Acta* 1994, 77, 2354.
- [8] W. P. Fehlhammer, F. Schoder, B. Weinberger, H. Stolzenberg, W. Beck, Z. Anorg. Allg. Chem. 2009, 635, , ,1367.
- a) W. P. Fehlhammer, K. Bartel, W. Petri, J. Organomet. Chem. 1975, 87, C34; b) W. P. Fehlhammer, K. Bartel, A. Völkl, D. Achatz, Z. Naturforsch. 1982, 37b, 1044; c) G. Zinner, W. P. Fehlhammer, Angew. Chem. 1985, 97, 990; Angew. Chem. Int. Ed. Engl. 1985, 24, 979; d) W. P. Fehlhammer, G. Zinner, M. Bakola-Christianopoulou, J. Organomet. Chem. 1987, 331, 193; e) U. Eckert, C. Robl, W. P. Fehlhammer, Organometallics 1993, 12, 3241.
- [10] W. P. Fehlhammer, H. Hoffmeister, U. Eckert, Z. Naturforsch. 1993, 48b, 1448.
- [11] K. Bartel, PhD-Thesis, University of Munich, 1976.
- [12] G. Zinner, M. Bakola-Christianopoulou, W. P. Fehlhammer in Organometallic Syntheses, (Eds.: R. B. King, J. J. Eisch) vol. 4, Elsevier, Amsterdam, 1988, pp. 82.
- [13] a) B. Weinberger, W. P. Fehlhammer, Angew. Chem. 1980, 92, 478; Angew. Chem. Int. Ed. Engl. 1980, 19, 480; b) B. Weinberger, W. P. Fehlhammer, Chem. Ber. 1985, 118, 42.
- [14] W. Hieber, E. Winter, E. Schubert, Chem. Ber. 1962, 95, 3070.
- [15] H. Bock, H. tom Dieck, Z. Naturforsch. 1966, 21b, 739.
- [16] K. A. O. Starzewski, H. tom Dieck, K. D. Franz, F. Hohman, J. Organomet. Chem. 1972, 42, C35.
- [17] F. Heydenreich, A. Mollbach, G. Wilke, H. Dreeskamp, E. G. Hoffmann, G. Schroth, K. Seevogel, W. Stempfle, *Isr. J. Chem.* 1972, *12*, 293.
- [18] F. R. Kreißl, C. G. Kreiter, E. O. Fischer, Angew. Chem. 1972, 84, 679; Angew. Chem. Int. Ed. Engl. 1972, 11, 643.
- [19] L. Knoll, J. Organomet. Chem. 1978, 148, C25.
- [20] E. Lindner, H. Berke, Chem. Ber. 1974, 107, 1360.
- [21] W. C. Kaska, D. K. Mitchell, R. F. Reichelderfer, J. Organomet. Chem. 1973, 47, 391.
- [22] a) W. P. Fehlhammer, R. Metzner, R. Kunz, *Chem. Ber.* 1994, 127, 321; b) W. P. Fehlhammer, R. Metzner, W. Sperber, *Chem. Ber.* 1994, 127, 631.
- [23] Due to partial hydrolysis of W(CO)₅CNCHPPh₃ the ¹H NMR resonance of the methin proton could not be assigned with certainty. The values for the coordination compound ([W(CO)₅CNCH₂PPh₃]PF₆: $\delta = 5.58$, ²*J*_{PH} = 8 Hz) compare well with those of the free isocyanide.
- [24] a) D. Achatz, *PhD-Thesis*, University of Erlangen-Nürnberg, 1982; b) Deprotonation by Na[N(SiMe₃₂₅₇₈₃Z. Naturforsch. 1976, 31b, 1019; c) H. Behrens, M. Moll, Z. Anorg. Allg. Chem. 1975, 416, 193.
- [25] W. P. Fehlhammer, A. Völkl, U. Plaia, G. Beck, Chem. Ber. 1987, 120, 2031.
- [26] G. Bittner, H. Witte, G. Hesse, Justus Liebigs Ann. Chem. 1968, 713, 1.
- [27] D. Achatz, M. A. Lang, A. Völkl, W. P. Fehlhammer, W. Beck, Z. Anorg. Allg. Chem. 2005, 631, 2339.
- [28] These data compare well with those of *cis*-[Pt(Cl)(Me)(PEt₃)₂]
 [δ(P1) -14.6, ¹J(Pt,P) = 1719 Hz (*trans*-Me); δ(P2) -8.7,
 ¹J(Pt,P) = 4179 Hz (*trans*-Cl)]: F. H. Allen, A. Pidcock, J. Chem. Soc. A **1968**, 2700.
- [29] M. A. Bennett, R. Bramley, J. B. Tomkins, J. Chem. Soc., Dalton Trans. 1973, 166.

- [30] K. Suzuki, H. Yamamoto, S. Kanie, J. Organomet. Chem. 1974, 73, 131.
- [31] H. C. Clark, L. E. Manzer, Inorg. Chem. 1972, 11, 2749.
- [32] S. H. Mastin, Inorg. Chem. 1974, 13, 1003.
- [33] A. M. van Leusen, personal communication.
- [34] W. P. Fehlhammer, F. Degel, H. Stolzenberg, Angew. Chem. 1981, 93, 184; Angew. Chem. Int. Ed. Engl. 1981, 20, 214.
- [35] T. Saegusa, Y. Ito, H. Kinoshiba, S. Tomita, J. Org. Chem. 1971, 36, 3316.
- [36] a) E. B. Dreyer, C. T. Lam, S. J. Lippard, *Inorg. Chem.* 1979, 18, 1904; b) M. P. Guy, J. T. Guy Jr, D. W. Bennett, *Organometallics* 1986, 5, 1696; c) F. E. Hahn, M. Tamm, *J. Organomet. Chem.* 1994, 467, 103.
- [37] J. Howard, P. Woodward, J. Chem. Soc., Dalton Trans. 1973, 1840.
- [38] a) R. Ugo, F. Conti, S. Cenini, R. Mason, G. B. Robertson, J. Chem. Soc., Chem. Commun. 1968, 1498; b) F. Cariati, R. Mason, G. B. Robertson, R. Ugo, J. Chem. Soc., Chem. Commun. 1967, 408.
- [39] R. Mason, C. W. Meek, Angew. Chem. Int. Ed. Engl. 1978, 17, 183.
- [40] A. Del Pra, G. Zanotti, A. Piazzesi, U. Belluco, R. Ros, Transition. Met. Chem. 1979, 4, 381.
- [41] D. R. Russell, P. A. Tucker, J. Chem. Soc., Dalton Trans. 1975, 2222.
- [42] J. A. Kaduk, J. A. Ibers, J. Organomet. Chem. 1977, 139, 199.
- [43] A. Del Pra, G. Zanotti, G. Bombieri, R. Ros, *Inorg. Chim. Acta* 1979, 36, 121.
- [44] M. A. Bennett, H.-K. Chee, G. B. Robertson, *Inorg. Chem.* 1979, 18, 1061.
- [45] A. Del Pra, E. Forsellini, G. Bombieri, R. A. Michelin, R. Ros, J. Chem. Soc., Dalton Trans. 1979, 1862.
- [46] a) M. J. S. Dewar, I. J. Turchi, J. Chem. Soc. Perkin Trans. 2, 1977, 724; b) E. C. Taylor, I. J. Turchi, Chem. Rev. 1979, 79, 181.
- [47] Organic nitrile imines were first prepared by Huisgen and coworkers: R. Huisgen, M. Seidel, J. Sauer, J. W. McFarland, G. Wallbillich, J. Org. Chem. 1959, 24, 892; R. Huisgen, M. Seidel, G. Wallbillich, H. Knupfer, Tetrahedron 1962, 18, 3; High-level ab initio MO calculations predict that the parent nitrile imine prefers a non planar, allenic structure: M. W. Wong, C. Wentrup, J. Am. Chem. Soc. 1993, 115, 7743.
- [48] B. Weinberger, G. Zinner, W. P. Fehlhammer, in *Organometallic Syntheses* (Eds.: R. B. King, J. J. Eisch), Vol. 4, Elsevier, Amsterdam, **1988**, pp. 87.
- [49] [Re(CO)₆]PF₆ was prepared analogous to [Re(CO)₆]BF₄: D. J. Darensbourg, J. A. Froehlich, J. Am. Chem. Soc. **1977**, 99, 4716.
- [50] a) L. Busetto, U. Belluco, R. J. Angelici, J. Organomet. Chem.
 1969, 18, 213; b) B. D. Dombek, R. J. Angelici, Inorg. Synth.
 1977, 17, 100.
- [51] W. P. Fehlhammer, W. A. Herrmann, K. Öfele, in *Handbuch der Präparativen Anorganischen Chemie* (Ed.: G. Brauer), Vol. III, Ferdinand Enke, Stuttgart, 3rd edn., 1981.
- [52] a) B. F. Hallam, P. L. Pauson, J. Chem. Soc. 1956, 3030; b) K. K. Joshi, P. L. Pauson, W. H. Stubbs, J. Organomet. Chem. 1963, 1, 51.
- [53] W. Strohmeier, Angew. Chem. 1964, 76, 873.
- [54] J. C. Hileman, D. K. Huggins, H. D. Kaesz, *Inorg. Chem.* 1962, 1, 933.
- [55] G. Sheldrick, SHELX-76, University of Cambridge, UK, 1976.
- [56] D. T. Cromer, J. T. Waber, International Tables for X-ray Crystallography, Kynoch Press, Birmingham, UK, 1974, vol. 4.
- [57] C. K. Johnson, ORTEP, Rep. ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, USA, 1976.

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