

# Reactivity of Silyl-Substituted Heterobimetallic Iron–Platinum Hydride Complexes towards Unsaturated Molecules, I Alkyne Insertions into the Platinum-Hydride Bond, Phosphane-Induced $\sigma$ -Alkenyl– $\mu$ -Vinylidene Rearrangements and Formation of $\mu$ -Isonitrile Complexes

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*Dedicated to Professor Helmut Werner on the occasion of his 65th birthday*

**Keywords:** Heterobimetallics / Hydride complexes / Alkenyl complexes /  $\mu$ -Isonitrile complexes / Silicon / Iron / Platinum

The heterobimetallic hydride complexes  $[(OC)_3Fe\{Si(OMe)_3\}(\mu-Ph_2PXPPH_2)Pt(H)(PR_3)]$  (**1a**: X = CH<sub>2</sub>, PR<sub>3</sub> = PPh<sub>3</sub>; **1b**: X = NH, PR<sub>3</sub> = PPh<sub>3</sub>; **1c**: X = CH<sub>2</sub>, PR<sub>3</sub> = PMePh<sub>2</sub>) have been prepared by the oxidative addition of  $[(OC)_3Fe(H)\{Si(OMe)_3\}(\eta^1-Ph_2PXPPH_2)]$  to  $[Pt(H_2C=CH_2)(PPh_3)_2]$  or by reaction of  $K[(OC)_3Fe\{Si(OMe)_3\}(\eta^1-dppm)]$  with *trans*- $[Pt(Ph)(H)(PPh_3)_2]$ . The solid-state structure of compound **1b** has been determined by single-crystal X-ray diffraction. 1-Alkynes such as methylpropiolate or phenylacetylene insert in a regiospecific manner into the Pt–H bond of **1** to yield the  $\sigma$ -alkenyl complexes  $[(OC)_3Fe\{\mu-Si(OMe)_2(OMe)\}(\mu-Ph_2PXPPH_2)Pt\{C(R)=CH_2\}]$  (**2a**: X = CH<sub>2</sub>, R = CO<sub>2</sub>Me; **2b**: X = NH, R = CO<sub>2</sub>Me; **3a**: X = CH<sub>2</sub>, R = Ph). Addition of the Pt–H bond of **3a** across the triple bond of  $[D_1]$ phenylacetylene affords  $[(OC)_3Fe\{\mu-Si(OMe)_2(OMe)\}(\mu-dppm)Pt\{C(Ph)=C(D)H\}]$  (**3a\***) having the deuteron *trans* to platinum (*cis* addition). This insertion reaction is accompanied by dissociation of the platinum-bonded PR<sub>3</sub> ligand and saturation of the vacant coordination site by a dative  $\mu-\eta^2-Si-O \rightarrow Pt$  interaction. When **3** is treated with PR<sub>3</sub> again, a subsequent phosphane-induced rearrangement leading to vinylidene-bridged complexes  $[(OC)_3Fe\{\mu-C=C(H)R'\}(\mu-Ph_2PXPPH_2)Pt(PR_3)]$  (**4a**: X = CH<sub>2</sub>, R' = Ph, PR<sub>3</sub> = PPh<sub>3</sub>; **4b**: X = NH, R' = Ph, PR<sub>3</sub> = PPh<sub>3</sub>; **4c**: X = CH<sub>2</sub>, R' = Ph,

PR<sub>3</sub> = PMePh<sub>2</sub>; **4d**: X = CH<sub>2</sub>, R' = *p*-tolyl, PR<sub>3</sub> = PPh<sub>3</sub>) occurs. Upon purging a solution of **3a** with carbon monoxide, the labile CO adduct  $[(OC)_3Fe\{Si(OMe)_3\}(\mu-dppm)-Pt(CO)\{C(Ph)=CH_2\}]$  **5a** is formed, addition of 2,6-xylyl isocyanide to **2a** and **3a** affords the isonitrile adducts  $[(OC)_3Fe\{Si(OMe)_3\}(\mu-dppm)Pt(CNxylyl)\{C(R)=CH_2\}]$  (**5b**: R = CO<sub>2</sub>Me; **5c**: R = Ph), respectively. When hydride complex **1a** is allowed to react with stoichiometric amounts of aromatic isonitriles, formal elimination of HSi(OMe)<sub>3</sub> occurs, yielding the heterodinuclear isonitrile-bridged complexes  $[(OC)_3Fe\{\mu-C=N-R\}(\mu-dppm)Pt(PPh_3)]$  (**6a**: R = 2,6-xylyl; **6b**: R = *o*-anisyl; **6c**: R = *p*-anisyl; **6d**: R = *p*-C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>) and the bis(isonitrile) complexes  $[(OC)_2(RN \equiv C)Fe\{\mu-C=N-R\}(\mu-dppm)Pt(PPh_3)]$  (**7a**: R = 2,6-xylyl; **7b**: R = *p*-anisyl). Single-crystal X-ray diffraction studies performed on **6a** and **6b** reveal that the molecular structures of these  $\mu$ -isonitrile complexes closely resemble the  $\mu$ -vinylidene complexes **4**. The two metal centers are bridged in a symmetric manner by strongly bent CNR ligands, the aromatic groups R being oriented towards the Fe(CO)<sub>3</sub> moiety. Electrophilic addition of HBF<sub>4</sub> to the basic nitrogen atom of the  $\mu$ -CNR ligand transforms **6** to the cationic  $\mu$ -aminocarbyne complexes  $[(OC)_3Fe\{\mu-CN(H)R\}(\mu-dppm)Pt(PPh_3)][BF_4]$  (**8a**: R = 2,6-xylyl; **8b**: R = *p*-anisyl; **8c**: R = *p*-C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>).

## Introduction

The insertion of small molecules such as CO, CO<sub>2</sub>, CNR, olefins, and alkynes into the metal–hydride bond of mononuclear transition metal complexes represents a fundamental reaction in organometallic chemistry, which is also of great relevance for homogenous catalysis.<sup>[1]</sup> The olefin insertion leading to transition metal alkyl complexes (as

well as the reverse reaction, the  $\beta$ -elimination), has especially been the subject of numerous experimental and theoretical studies.<sup>[2]</sup> The insertion of alkynes into the metal–hydride bond, affording vinyl or alkenyl complexes, is very much related to the olefin insertion. In general, it is assumed that alkene and alkyne insertions proceed in most cases via a cyclic four-membered transition state. The insertion of acetylenes and isonitriles R–N $\equiv$ C (which also possess a reactive triple bond) across the Pt–H bond of mononuclear platinum complexes has been examined in detail by Clark and co-workers.<sup>[3][4]</sup>

In the course of our investigations into the insertion and activation of small molecules by heterobimetallic complexes, we were interested in studying the insertion of such molecules into the Pt–H bond of heterodinuclear systems of the type  $L_nM-Pt(H)L_2$ , containing two *different* metal centers linked by a metal–metal bond. The influence of

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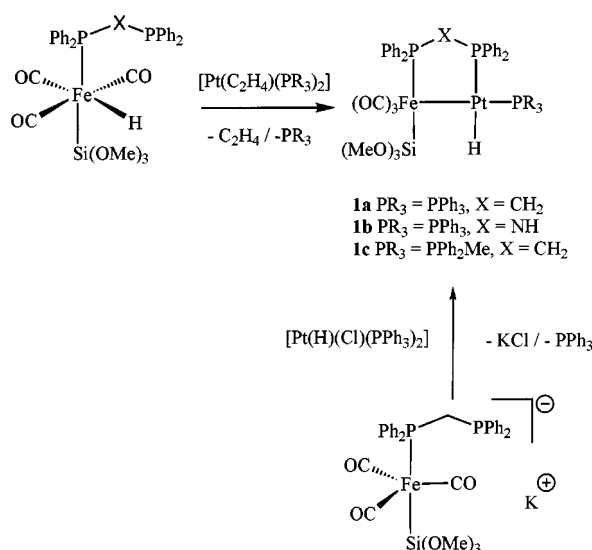
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the second adjacent metal center close to a square planar platinum(II) moiety on the regio- and site selectivity of this important reaction was of special interest. Here we report on the reactivity of 1-alkynes and aromatic isonitriles towards heterobimetallic iron–platinum hydride complexes and their transformation into  $\sigma$ -alkenyl,  $\mu$ -vinylidene, and  $\mu$ -isonitrile complexes, respectively.

## Results and Discussion

For our studies on the reactivity of heterometallic hydride complexes towards unsaturated molecules, the alkoxy-silyl-substituted dinuclear complex  $[(OC)_3Fe\{Si(OMe)_3\}(\mu\text{-dppm})Pt(H)(PPh_3)]$  **1a** appeared to be a promising system. Compound **1a** has been previously prepared by oxidative addition of the hydrido-silyl complex  $[(OC)_3Fe(H)\{Si(OMe)_3\}(\eta^1\text{-dppm})]$  to the  $Pt^0$  complex  $[Pt(H_2C=CH_2)(PPh_3)_2]$ .<sup>[5]</sup> Alternatively, this starting material can also be synthesized by the reaction of the metallate  $K[(CO)_3Fe\{Si(OMe)_3\}(\eta^1\text{-dppm})]$ <sup>[6a]</sup> with *trans*- $[Pt(Cl)(H)(PPh_3)_2]$  in 86% isolated yield (Scheme 1). In order to fine-tune the steric and electronic environment around the square-planar platinum center, we also prepared the bis(diphenylphosphanylamine)-bridged derivatives  $[(OC)_3Fe\{Si(OMe)_3\}(\mu\text{-dppa})Pt(H)(PPh_3)]$  **1b** and  $[(OC)_3Fe\{Si(OMe)_3\}(\mu\text{-dppm})Pt(H)(PMePh_2)]$  **1c** as precursors for reactivity studies (Scheme 1). All derivatives of **1** can be handled in the solid state in air without significant decomposition. They show only moderate solubility in aromatic solvents, but are fairly soluble in  $CHCl_3$  and  $CH_2Cl_2$ .



Scheme 1

Comparative IR studies indicate that the dppa-backbone of **1b** slightly reduces the electron density of the bimetallic system, whereas due to the better  $\sigma$ -donor capacity of  $PPh_2Me$  relative to  $PPh_3$ , a slight shift of the  $\nu(CO)$  frequencies to lower wavenumbers is noticeable for **1c**. A weak absorption band observed at  $2119\text{ cm}^{-1}$  is assigned to the  $\nu(PtH)$  stretch. The pattern of the hydride resonances in the

$^1H$ -NMR spectra are virtually identical for all derivatives of **1** and consistent with a terminal platinum-bonded hydride ligand. For example, in the spectrum of **1b**, a doublet of triplets is observed at  $\delta = -4.09$  due to a strong  $P_{trans}\text{-H}$  coupling of  $^2J = 209\text{ Hz}$  and an accidentally identical  $P_{cis}\text{-H}$  and  $P\text{-H}$  coupling of  $^2J$  and  $^3+4J = 16\text{ Hz}$ . In addition, the hydride signal is flanked by platinum satellites with a  $Pt\text{-H}$  coupling of  $^1J = 662\text{ Hz}$ . For all new dppa-spanned compounds presented in this paper, a pronounced downfield shift is observed for the dppa phosphorus nuclei in the  $^{31}P\{^1H\}$ -NMR spectra compared to those of the dppm-spanned analogues. Thus, the AMX-type spectrum of **1b** consists of three mutually coupled phosphorus resonances. The doublet of doublets due to the dppa-phosphorus on iron at  $\delta = 119.7$  is strongly coupled [ $^{2+3}J(P^1\text{-}P^2) = 138\text{ Hz}$ ] to the dppa-phosphorus on platinum, whose resonance is found at  $\delta = 81.7$ . Further splitting results from the platinum-bonded  $PPh_3$  ligand at  $\delta = 29.9$  with couplings of 12 and 63 Hz, respectively. All resonances are flanked by  $^{195}Pt$  satellites, the  $Pt\text{-P}$  couplings of which ( $J = 87, 2884$ , and  $3503\text{ Hz}$ ) are also evident in the  $^{195}Pt$ -NMR spectrum giving rise to a doublet of doublets of doublets centered at  $\delta = -2999$ .

## Crystal Structure of

### $[(OC)_3Fe\{Si(OMe)_3\}(\mu\text{-dppa})Pt(H)(PPh_3)]$

The molecular structure of the dinuclear hydride complex **1b** including the atom numbering scheme is shown in Figure 1. Suitable crystals were obtained by slow diffusion of hexane into a saturated dichloromethane solution of **1b**. The iron and platinum centers are linked by a dppa bridge and a metal–metal bond. The Fe–Pt separation of  $2.670(2)\text{ \AA}$  is almost identical to that observed in the trifluorosilyl-substituted complex  $[(OC)_3Fe\{SiF_3\}(\mu\text{-dppm})Pt(H)(PPh_3)]$  [ $2.661(1)\text{ \AA}$ ].<sup>[7]</sup> The coordination geometry around the Fe atom may be viewed as a distorted octahedral, consistent with a formal  $Fe(d^7)\text{-}Pt(d^9)$  situation. The silyl ligand, which is situated *trans* to  $P(1)$  [ $Si\text{-}Fe\text{-}P(1)$   $167.71(4)^\circ$ ] has a Fe–Si bond length of  $2.298(2)\text{ \AA}$ , which is in the typical range found for other heterometallic systems having a terminal  $Si(OMe)_3$  unit. For example, a Fe–Si bond length of  $2.271(4)\text{ \AA}$  has been found in  $[(OC)_3Fe\{Si(OMe)_3\}(\mu\text{-dppm})Cu(PPh_3)]$ .<sup>[6]</sup> Three meridional arranged carbonyl ligands complete the environment of the iron center. The square-planar coordination geometry around the platinum center involves the Fe atom, two phosphorus atoms (one from the dppa-bridge [ $Pt\text{-}P(2)$   $2.304(2)\text{ \AA}$ ], the second one from the  $PPh_3$  ligand [ $Pt\text{-}P(3)$   $2.228(2)\text{ \AA}$ ] and a hydride ligand [ $Pt\text{-}H(1)$   $1.544(4)\text{ \AA}$ ]. The root mean square deviation from the plane passing through Fe,  $P(2)$ ,  $P(3)$ , and  $H(1)$  amounts to  $0.102\text{ \AA}$ . Due to the good data set collected for **1b**, some electron density could successfully be refined as a *terminal* hydride position. This is consistent with the other spectroscopic results obtained (see above). The hydride ligand is quite close to one of the oxygen atoms of the  $Si(OMe)_3$  group [ $d(O(6)\cdots H(1))$   $2.45(4)\text{ \AA}$ ]. Similar

close contacts were already observed for  $[(OC)_3Fe(SiF_3)(\mu-dppm)Pt(H)(PPh_3)]$ ,<sup>[7]</sup> where a weak intramolecular interaction between the hydride ligand and two F atoms of the  $SiF_3$  ligand (bifurcated hydrogen bond with  $H\cdots F$  2.39(7) and 2.50(6) Å) was even retained in solution. As noticed for the latter hydride complex, the Pt–P(2) bond length of **1b** [2.304(2) Å] is significantly longer than that of Pt–P(3) [2.228(2) Å], which might reflect the high *trans* influence of the hydride ligand.

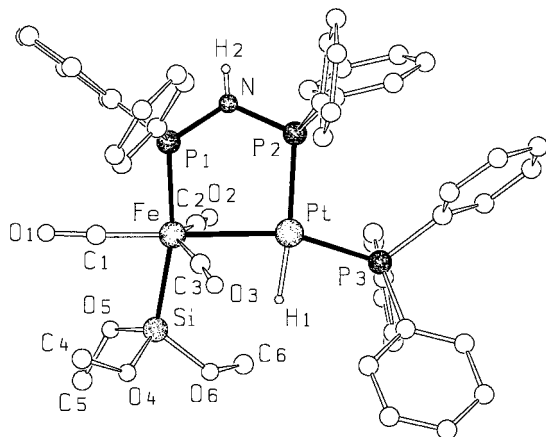
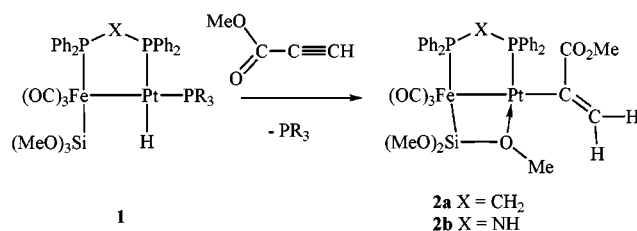


Figure 1. View of the crystal structure of **1b** showing the atom numbering scheme; selected bond lengths [Å] and angles [°]: Fe–Pt 2.670(2), Fe–Si 2.298(2), Fe–P(1) 2.203(2), Pt–P(2) 2.304(2), Pt–P(3) 2.228(2), Fe–C(1) 1.746(1), Fe–C(2) 1.756(4), Fe–C(3) 1.757(4), C(1)–O(1) 1.44(4), C(2)–O(2) 1.47(4), C(3)–O(3) 1.153(4), P(1)–N 1.684(3), P(2)–N 1.681(3), N–H(2) 0.81(4); Si–Fe–Pt 167.71(4), H(1)–Pt–Fe 80.5(13), H(1)–Pt–P(3) 79.8(13), Fe–Pt–Si 100.61(6), C(1)–Fe–Si 80.11(13), C(2)–Fe–Si 85.85(12), C(3)–Fe–Si 86.01(13), O(1)–C(1)–Fe 177.6(3), O(2)–C(2)–Fe 177.3(3), O(3)–C(3)–Fe 175.2(4), C(1)–Fe–P(1) 87.67(13), C(2)–Fe–P(1) 96.68(12), C(3)–Fe–P(1) 99.79(13), C(1)–Fe–Pt 179.28(12), C(2)–Fe–Pt 72.47(13), C(3)–Fe–Pt 68.85(13), P(1)–Fe–Pt 91.61(6), P(2)–Pt–P(3) 105.60(6), Fe–Pt–P(2) 93.86(6), Fe–Pt–P(3) 157.68(3), P(1)–N–P(2) 119.8(2).

## Reactivity towards 1-Alkynes

Upon addition of a threefold excess of methyl propiolate to a  $CH_2Cl_2$  solution of **1a**, quantitative insertion into the platinum–hydride bond occurred within 4 h at ambient temperature leading to the heterobimetallic  $\sigma$ -alkenyl complex  $[(OC)_3Fe\{\mu-Si(OMe)_2(OMe)\}(\mu-dppm)Pt\{C(CO_2Me)=CH_2\}]$  **2a** (Scheme 2). Elemental analyses and spectroscopic data showed that the alkyne insertion is accompanied by dissociation of the platinum-bonded  $PR_3$  ligand. The vacant coordination site on the platinum center is electronically saturated by a dative interaction of a methoxy group of the trimethoxysilyl ligand, forming a four-membered Fe–Si–O→Pt cycle. This feature has been studied in detail, both in solution and in the solid state.<sup>[5,8,9]</sup> The  $\sigma$ -alkenyl complex **2a** is also formed using the  $Ph_2MeP$ -substituted derivative **1c** as starting material. In an analogous manner, the dppa-bridged insertion product  $[(OC)_3Fe\{\mu-Si(OMe)_2(OMe)\}(\mu-dppa)Pt\{C(CO_2Me)=CH_2\}]$  **2b** is formed after addition of methyl propiolate to **1b**. Elemental

analyses and spectroscopic data indicated that a triphenylphosphane oxide ligand, which stems from partial oxidation of the liberated  $PPh_3$ , is probably bonded by a hydrogen bond to the N–H group of the dppa ligand of **2b**. In all the cases, insertion occurs in a regioselective manner, affording the isomer with the ester group attached on the  $\alpha$ -carbon. The new yellow compounds, which were moderately soluble in diethyl ether, were stable in solution for longer periods and thus permitted extensive multinuclear NMR measurements to be made (see Experimental Section).

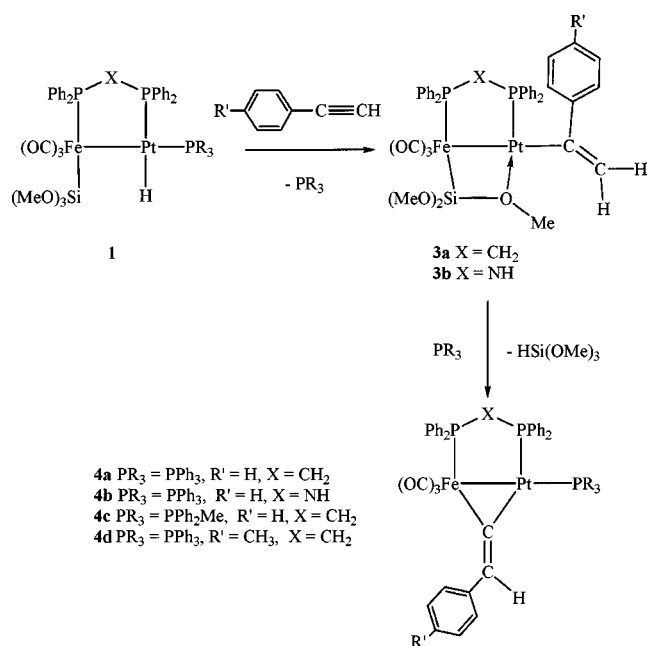


Scheme 2

A more complicated reaction occurred, when **1a** was treated with the less reactive phenylacetylene.  $^{31}P$ -NMR monitoring of the course of the reaction revealed that 40 min after addition of 10 equivalents of phenylacetylene to **1a**, a ca. 60:40 mixture of unchanged **1a** and insertion product  $[(OC)_3Fe\{\mu-Si(OMe)_2(OMe)\}(\mu-dppm)Pt\{C(Ph)=CH_2\}]$  **3a** was formed. The latter gave rise to an AX-type spectrum consisting of a doublet at  $\delta = 61.2$  due to the phosphorus on iron, which is coupled to the platinum-bonded phosphorus at  $\delta = 6.9$  with  $^{2+3}J(P^1-P^2) = 41$  Hz. The latter resonance shows a very large  $^1J$  coupling of 5010 Hz to the  $^{195}Pt$  nucleus, whereas the former displays a small  $^{2+3}J(Pt-P)$  coupling of 61 Hz. In addition, a broad signal centered at  $\delta = -4.2$  due to the liberated  $PPh_3$  is observed. After several hours, the intensity of the signals due to **3a** grows, whereas that of the hydride complex **1a** diminishes. In addition, a third set of signals emerges consisting of three mutually coupled resonances centered at  $\delta = 63.0, 43.6$ , and  $22.2$ , whose chemical shifts and couplings are identical to those of the vinylidene-bridged complex  $[(OC)_3Fe\{\mu-C=C(H)Ph\}(\mu-dppm)Pt(PPh_3)]$  **4a**. Compound **4a** has been prepared recently by the reaction of the vinylidene-bridged complex  $[(OC)_3Fe\{\mu-C=C(H)Ph\}(\mu-dppm)Pt(CO)]$  with triphenylphosphane and was structurally characterized by an X-ray diffraction study.<sup>[10]</sup> Within 24 h, compound **1a** had been completely consumed and only the  $^{31}P$  resonances of **3a** and **4a** were detected in a ca. 10:90 ratio. The quantitative transformation of the intermediate **3a** to **4a** may have been prevented by partial oxidation of the liberated  $PPh_3$ , since a singlet at  $\delta = 29.5$  due to minor amounts of  $O=PPh_3$  was also detected in the  $^{31}P$ -NMR spectrum.

In a similar manner, phenylacetylene inserted into the Pt–H bond of **1b** to yield first the dppa-bridged  $\sigma$ -alkenyl complex  $[(OC)_3Fe\{\mu-Si(OMe)_2(OMe)\}(\mu-dppa)Pt\{C(Ph)=CH_2\}]$  **3b** as an intermediate, which was characterized only

in solution [ $^{31}\text{P}$   $\delta$  = 111.2 P(Fe), 45.5 P(Pt),  $^{2+3}J(\text{P}^1\text{-P}^2)$  = 45 Hz;  $^{195}\text{Pt}$   $\delta$  = -2345, dd,  $^1J(\text{Pt-P})$  = 5524 Hz,  $^{2+3}J(\text{Pt-P})$  = 55 Hz]. The latter was finally transformed in situ to the new stable  $\mu$ -vinylidene complex  $[(\text{OC})_3\text{Fe}\{\mu\text{-C}=\text{C}(\text{H})\text{Ph}\}(\mu\text{-dppa})\text{Pt}(\text{PPh}_3)]$  **4b** after reaction with  $\text{PPh}_3$ . The derivatives  $[(\text{OC})_3\text{Fe}\{\mu\text{-C}=\text{C}(\text{H})\text{Ph}\}(\mu\text{-dppm})\text{Pt}(\text{PMePh}_2)]$  **4c** and  $[(\text{OC})_3\text{Fe}\{\mu\text{-C}=\text{C}(\text{H})p\text{-tolyl}\}(\mu\text{-dppm})\text{Pt}(\text{PPh}_3)]$  **4d** were prepared according to Scheme 3 by reaction of **1c** and **1a** with phenylacetylene and *p*-tolylacetylene, respectively.



Scheme 3

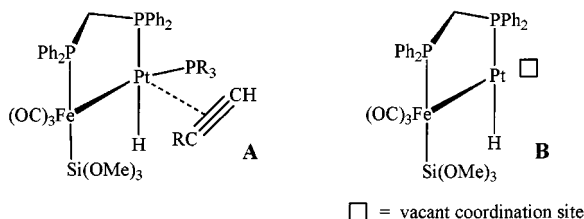
In order to assign the stereochemistry of the alkenyl group of **3a** unambiguously, we isolated this complex by stopping the reaction before all of **3a** had been converted into **4a**. Due to its solubility in an ether/hexane mixture, the alkenyl complex could be separated from unchanged **1a** and the final product **4a** by extraction. The geminal position of the alkenyl hydrogen atoms can be deduced from the  $^1\text{H}$ -NMR spectrum, which shows no resolved coupling between these two protons. The broadened singlet at  $\delta$  = 5.96 is assigned to the (*E*)-proton in a *trans* position to the platinum center, since it displays a strong Pt-H coupling of  $^3J$  = 108 Hz, whereas the (*Z*)-proton signal at  $\delta$  = 5.09 shows a coupling constant of  $J$  = 58 Hz only. Similar magnitudes and coupling patterns have been reported for mononuclear complexes of the type  $[\text{L}_n\text{Pt}\{\text{C}(\text{R})=\text{CH}_2\}]$ .<sup>[11]</sup> For regioisomer  $[\text{L}_n\text{Pt}\{(E)\text{-C}(\text{H})=\text{CH}(\text{Ph})\}]$ , a *trans* coupling  $^3J(\text{H-H})$  of ca. 17 Hz should be expected, while regioisomer  $[\text{L}_n\text{Pt}\{(Z)\text{-C}(\text{H})=\text{CH}(\text{Ph})\}]$  should exhibit a *cis* coupling  $^3J(\text{H-H})$  of ca. 10 Hz.<sup>[11]</sup> Consistent with a rigid Fe-Si-O→Pt unit, two distinct signals in a 2:1 ratio at  $\delta$  = 3.76 and 3.65 due to different methoxy groups are also observed. Employing  $[\text{D}_1]$ phenylacetylene (98%) as substrate, only the resonance of the (*Z*)-vinyl proton is observed in the  $^1\text{H}$ -NMR spectrum of the deuterated complex

**3a\***. The resonance of the (*E*)-vinyl deuteron is found in the  $^2\text{H}$ -NMR spectrum at  $\delta$  = 6.07. This isotopic labeling experiment proves that insertion of  $[\text{D}_1]$ phenylacetylene occurred in a *cis* manner. The  $^{13}\text{C}\{^1\text{H}\}$  NMR recorded at 268 K (see Experimental Section) further corroborates our structural proposal for **3a** possessing the same stereochemistry at the alkenyl group as  $[(\text{OC})_3\text{Fe}\{\mu\text{-Si}(\text{OMe})_2(\text{OMe})\}(\mu\text{-Ph}_2\text{PXPPH}_2)\text{Pt}\{\text{C}(\text{CO}_2\text{Me})=\text{CH}_2\}]$  **2**.

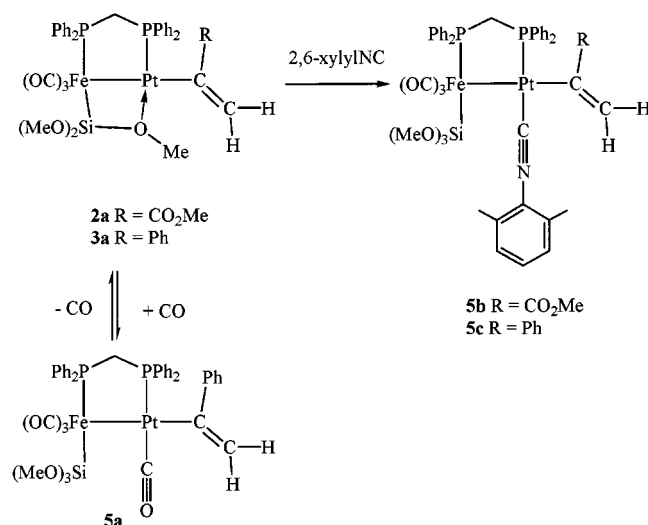
The subsequent  $\sigma$ -alkenyl- $\mu$ -vinylidene rearrangement in the presence of  $\text{PR}_3$ , observed for the alkenyl complexes  $[(\text{OC})_3\text{Fe}\{\mu\text{-Si}(\text{OMe})_2(\text{OMe})\}(\mu\text{-Ph}_2\text{PXPPH}_2)\text{Pt}\{\text{C}(\text{R})=\text{CH}_2\}]$ , seemed to depend in a sensitive manner on the electronic behaviour of the organic group R at the  $\alpha$ -carbon atom of the alkenyl ligand. When  $[(\text{OC})_3\text{Fe}\{\mu\text{-Si}(\text{OMe})_2(\text{OMe})\}(\mu\text{-dppm})\text{Pt}\{\text{C}(\text{CO}_2\text{Me})=\text{CH}_2\}]$ , possessing a strong electron-withdrawing  $\text{CO}_2\text{Me}$  group, was treated with two equivalents of  $\text{PPh}_3$  or  $\text{PMePh}_2$ , no  $\sigma$ -alkenyl- $\mu$ -vinylidene rearrangement was observed even after several hours. However, this transformation could be induced by addition of  $\text{PPh}_3$  to **3a**. In an NMR experiment, performed in  $\text{CDCl}_3$  solution, **3a** was gradually converted into the  $\mu$ -vinylidene complex **4a** within 5 h after addition of three equivalents of  $\text{PPh}_3$ . A somewhat related phosphane-induced transformation has recently been studied on heterodinuclear acyl complexes of the type  $[(\text{OC})_3\text{Fe}\{\mu\text{-Si}(\text{OMe})_2(\text{OMe})\}(\mu\text{-dppm})\text{Pt}\{\text{C}(\text{O})\text{R}\}]$  (R = Me, Et). The latter acyl complexes were converted into  $\mu$ -silyloxycarbene complexes  $[(\text{OC})_3\text{Fe}\{\mu\text{-C}(\text{R})\text{OSi}(\text{OMe})_3\}(\mu\text{-dppm})\text{Pt}(\text{PR}'_3)]$  after addition of phosphanes or phosphites; the rate of the rearrangement depended on the basicity of  $\text{PR}'_3$ .<sup>[12]</sup> In the case of **3a**, the phosphane-promoted rearrangement occurs with concomitant reductive elimination of  $\text{HSi}(\text{OMe})_3$ , as proved by NMR monitoring. Trimethoxysilane elimination has previously been observed upon treatment of the hydrido complex  $[(\text{OC})_3\text{Fe}\{\mu\text{-Si}(\text{OMe})_2(\text{OMe})\}(\mu\text{-dppm})\text{Rh}(\text{H})(\text{Cl})]$  with carbon monoxide and during the reaction of  $[(\text{OC})_3\text{Fe}(\text{H})\{\text{Si}(\text{OMe})_3\}(\eta^1\text{-dppm})]$  with *fac*- $[\text{Re}(\text{CO})_3((\text{THF})(\mu\text{-Br}))_2]$  affording the bromide-bridged complex  $[(\text{OC})_3\text{Fe}(\mu\text{-Br})(\mu\text{-dppm})\text{Re}(\text{CO})_3]$ .<sup>[13]</sup> Mechanistically, this alkenyl-vinylidene rearrangement probably involves intramolecular migration of a hydrogen atom from the  $\beta$ -carbon to the  $\alpha$ -carbon of the alkenyl ligand, which forms the  $\beta$ -carbon of the vinylidene bridge after rearrangement. Related hydridovinylidene-alkenyl rearrangement involving  $\alpha$ -hydrogen shifts have been investigated experimentally and theoretically in mononuclear tantalum and ruthenium complexes.<sup>[14]</sup> It should be noted that in the latter example, phenylacetylene has been inserted into the Ru-H bond of  $[\text{RuHX}(\text{H}_2)(\text{PR}_3)_2]$ , leading to an alkenyl intermediate  $[\text{L}_n\text{Ru}-\text{C}(\text{H})=\text{C}(\text{H})\text{Ph}]$  bearing the phenyl group on the  $\beta$ -carbon atom.<sup>[14b]</sup> An open question remains as to whether alkyne coordination on platinum prior to insertion into the Pt-H bond is associative or dissociative (Scheme 4). Both the initial formation of a penta-coordinated intermediate **A** or the initial dissociation of a ligand like  $\text{PPh}_3$  (creating a vacant coordination site as in **B**) are well established pathways for migratory insertion reactions occurring in platinum com-



plexes.<sup>[15]</sup> We performed the reaction of **1a** with phenylacetylene in the presence of three equivalents of PPh<sub>3</sub> to investigate the role of the phosphane concentration on the acetylene insertion rate. Unfortunately, progressive fragmentation of the Fe–Pt bond occurred, leading to several mononuclear species, among them *trans*-[Fe(CO)<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>].



Scheme 4



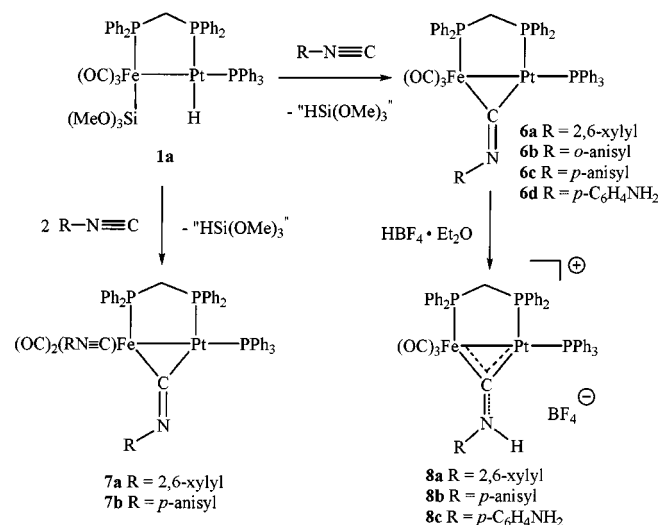
Scheme 5

We have recently shown that CO instantaneously reacts with dinuclear alkyl complexes of the type [(OC)<sub>3</sub>Fe{μ-Si(OMe)<sub>2</sub>(OMe)}(μ-dppm)PtR] (R = Me, Et, norbornyl) to give, by opening of the μ-η<sup>2</sup>-Si–O bridge, the CO adducts [(OC)<sub>3</sub>Fe{Si(OMe)<sub>3</sub>}(μ-dppm)Pt(CO)R]. These intermediates rearrange due to a CO migratory insertion reaction into the Pt–C bond to the stable acyl complexes [(OC)<sub>3</sub>Fe{μ-Si(OMe)<sub>2</sub>(OMe)}(μ-dppm)Pt{C(=O)R}].<sup>[8]</sup> However, no spectroscopic change was noticed upon purging a solution of **2a** with a gentle stream of CO for 2 h. In contrast, **3b** afforded the CO adduct [(OC)<sub>3</sub>Fe{Si(OMe)<sub>3</sub>}(μ-dppm)Pt(CO){C(Ph)=CH<sub>2</sub>}] **5a**, as evidenced by the appearance of a new ν(CO) vibration due to the Pt-bonded carbonyl ligand at 2088 cm<sup>−1</sup> in the IR spectrum, and the emergence of a new AX pattern in the <sup>31</sup>P-NMR spectrum centered at δ = 60.8 and 15.0 with a P–P coupling constant of <sup>2+3</sup>J = 78 Hz and a P–Pt coupling constant of <sup>1</sup>J = 3414 Hz. Since **5a** readily lost the carbonyl ligand under reduced pressure regenerating **3a**, this complex could not be isolated. In the presence of stoichiometric amounts of 2,6-xylyl isocyanide, the dative Pt–OMe bond was instantaneously broken and the isonitrile adducts

[(OC)<sub>3</sub>Fe{Si(OMe)<sub>3</sub>}(μ-dppm)Pt(CNxyly){C(R)=CH<sub>2</sub>}] (**5b**: R = CO<sub>2</sub>Me; **5c**: R = Ph) were isolated as stable yellow solids. In addition to the three ν(CO) stretches of the Fe(CO)<sub>3</sub> unit, the IR spectra of **5b/5c** displayed a strong vibration at 2181/2176 cm<sup>−1</sup>, consistent with a terminal bonding mode of the isonitrile ligand at the platinum center.

### Reactivity of **1** towards Isonitriles

The insertion of isonitriles into the Pt–H bond of platinum hydrido complexes leading to formimidoyl complexes [L<sub>n</sub>Pt{C(H)=NR}] is a well established reaction.<sup>[3a,16]</sup> With the anticipation of inserting isonitriles C≡N–R into the Pt–H bond of **1**, we reacted **1a** with a stoichiometric amount of aromatic isonitriles in CH<sub>2</sub>Cl<sub>2</sub> to yield heterodinuclear formimidoyl complexes.<sup>[17a]</sup> Surprisingly, no formimidoyl complexes were isolated. Instead, the isonitrile-bridged bimetallic complexes [(CO)<sub>3</sub>Fe(μ-C=N)(μ-dppm)Pt(PPh<sub>3</sub>)] (**6a**: R = 2,6-xylyl, **6b**: R = *o*-anisyl, **6c**: R = *p*-anisyl, **6d**: R = *p*-aminophenyl) were obtained as stable orange-yellow solids (Scheme 6). The NMR spectra of **6** resemble those of the structurally related dppm-bridged μ-vinylidene complexes **4a** and **4c**. Indicative of a bridging bent isonitrile ligand are the IR spectra of **6**, which displayed a broadened ν(C=N) vibration of medium intensity in the range between 1667–1669 cm<sup>−1</sup>.



Scheme 6

### Crystal Structures of [(OC)<sub>3</sub>Fe(μ-C=N–R)(μ-dppm)Pt(PPh<sub>3</sub>)]

In heterobimetallic μ-isonitrile complexes M(μ-C=N–R)M' possessing a bent C=N–R arrangement, two isomeric forms are a priori conceivable, which differ in the relative orientation of R towards M or M'. In order to elucidate unambiguously the orientation of R and the degree of inclination, the molecular structure of

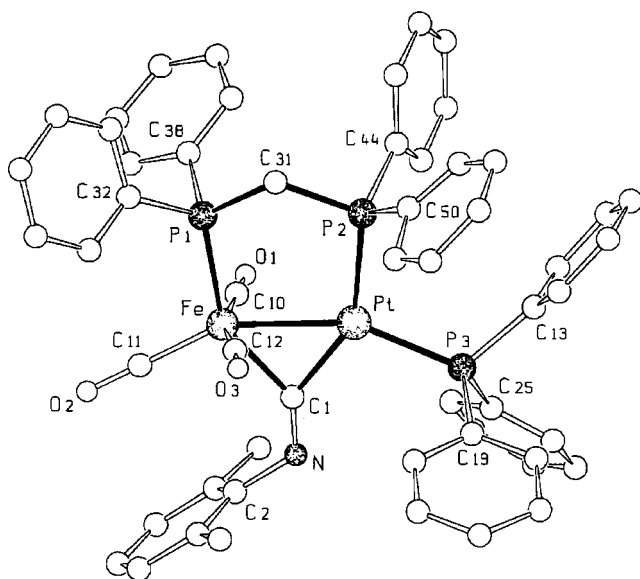


Figure 2. View of the crystal structure of **6a** showing the atom numbering scheme; selected bond lengths [Å] and angles [°]: Fe–Pt 2.522(4), Fe–P(1) 2.212(5), Pt–P(2) 2.297(5), Pt–P(3) 2.243(3), Pt–C(1) 1.994(8), Fe–C(1) 1.988(8), Fe–C(10) 1.768(9), Fe–C(11) 1.761(11), Fe–C(12) 1.836(11), C(1)–N 1.202(11), C(2)–N 1.425(14), C(10)–O(1) 1.138(12), C(11)–O(2) 1.129(13), C(12)–O(3) 1.066(12), P(1)–C(31) 1.851(9), P(2)–C(31) 1.831(9), C(1)–N(1)–C(2) 122.1(8), Pt–C(1)–Fe 78.6(3), Fe–Pt–C(1) 50.6(2), C(1)–Fe–Pt 50.8(2), C(1)–Fe–P(1) 147.7(3), C(1)–Pt–P(2) 147.7(2), C(1)–Pt–P(3) 105.7(3), P(1)–Fe–Pt 97.20(14), P(2)–Pt–P(3) 106.4(2), Fe–Pt–P(3) 155.94(9), P(1)–C(31)–P(2) 114.3(5)

**6a** · 1.5 CH<sub>2</sub>Cl<sub>2</sub> shown in Figure 2 has been determined by a single-crystal X-ray diffraction study. Suitable crystals were obtained by layering a saturated dichloromethane solution with Et<sub>2</sub>O. The iron and platinum centers are linked by a dppm bridge and a metal–metal bond, whose Fe–Pt separation of 2.552(4) Å is almost identical to that of the vinylidene complex [(OC)<sub>3</sub>Fe{μ-C=C(H)Ph}(μ-dppm)Pt(PPh<sub>3</sub>)] [2.5503(8) Å].<sup>[10]</sup> Also, the other structural features are very reminiscent of the molecular structure of the latter compound. The bridging isonitrile ligand is symmetrically situated between the metals, with Fe–C(1) and Pt–C(1) distances of 1.988(8) and 1.994(8) Å, respectively. The length of the C(1)–N double bond of 1.20(1) Å is comparable to that of the W–Pt complex [(OC)<sub>4</sub>W(μ-C=NCH<sub>2</sub>SO<sub>2</sub>-*p*-tolyl)(μ-dppa)Pt(PPh<sub>3</sub>)] [1.229(12) Å]<sup>[17b,17d]</sup> and to those reported for some homobimetallic isonitrile-bridged systems.<sup>[19]</sup> The C(1)–N–C(2) angle is extremely bent [122.1(8)°], the xylyl group being oriented towards the Fe(CO)<sub>3</sub> moiety. A comparable inclination with an average C–N–C angle of 123.1°, was found for the μ-C=N–Et ligands of [(EtNC)<sub>3</sub>Fe–μ-CNEt<sub>3</sub>Fe(CNEt<sub>3</sub>)]<sup>[18d]</sup> whereas for most structurally characterized bent μ-CNR systems, C–N–C angles in the range between 130–133° have been documented.<sup>[18]</sup> For example, a C–N–C angle of 131.7(3)° has been determined for the bridging xylyl isocyanide ligands of the dinuclear compound *trans*-[η<sup>5</sup>-CpFe(CN–2,6-xylyl)(μ-CN–2,6-xylyl)]<sub>2</sub>.<sup>[18g]</sup> An unusual, widened C–N–C angle of 149.4(23) Å has been observed recently in a Pd(μ-CN*t*Bu)(μ-SiR<sub>2</sub>)Pd

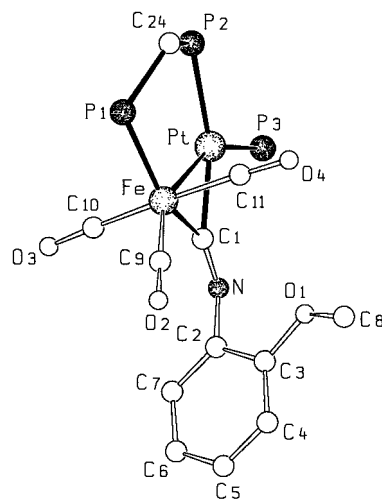


Figure 3. Perspective view of the core structure of **6b** along the Fe–Pt axis showing the atom numbering scheme. The phenyl groups are omitted for clarity; selected bond lengths [Å] and angles [°]: Fe–Pt 2.522(2), Fe–P(1) 2.226(3), Pt–P(2) 2.313(3), Pt–P(3) 2.259(3), Pt–C(1) 2.013(10), Fe–C(1) 1.991(10), Fe–C(10) 1.772(14), Fe–C(11) 1.789(13), Fe–C(9) 1.777(13), C(1)–N 1.92(12), C(2)–N 1.406(14), C(9)–O(2) 1.113(14), C(10)–O(3) 1.16(2), C(11)–O(4) 1.143(14), P(1)–C(24) 1.832(9), P(2)–C(24) 1.839(9), C(1)–N(1)–C(2) 127.2(9), Pt–C(1)–Fe 79.2(4), Fe–Pt–C(1) 50.0(3), C(1)–Fe–Pt 50.8(3), C(1)–Fe–P(1) 143.4(3), C(1)–Pt–P(2) 148.4(3), C(1)–Pt–P(3) 102.0(3), C(1)–Fe–C(9) 106.3(4), C(1)–Fe–C(10) 82.3(5), C(1)–Fe–C(11) 88.7(4), P(1)–Fe–Pt 93.63(8), P(2)–Pt–P(3) 109.61(10), Fe–Pt–P(3) 151.84(8), P(1)–C(24)–P(2) 112.4(5)

complex.<sup>[18l,18m]</sup> We believe that this strong bending observed in **6a** may be caused by electronic factors, since the π-acceptor capacity of bridging isonitrile ligands is correlated to the degree of inclination.<sup>[19]</sup> Because the isonitrile complexes **6** represent electron-rich systems due to the presence of two metal centers in low oxidation states with three phosphorus donors as ligands, a strongly bent isonitrile bridge behaving as a good π-acceptor can at least partially compensate for the high electron density by back-bonding into π\*-orbitals. Note that a bridging vinylidene unit, as encountered in **4**, also behaves as an efficient π-acceptor ligand.<sup>[20][21]</sup> As already discussed for the molecular structures of the μ-vinylidene complex **4a**<sup>[10]</sup> and the cationic μ-aminocarbene complex [(OC)<sub>3</sub>Fe(μ-CN(H)*o*-anisyl)(μ-dppa)Pt(PPh<sub>3</sub>)]<sup>[17c,17d]</sup> the orientation towards the carbonyl fragment is imposed by the *steric bulk* of the triphenylphosphane ligand on platinum, which would otherwise interfere unfavorably with the 2,6-xylyl group.

As can be seen from Figure 3, which shows the core structure of **6b** along the Fe–Pt axis, the structural features of the *o*-anisyl isocyanide bridged derivative **6b** are similar to those of **6a**. As found in **6a**, the aromatic group of the isonitrile bridge is bent and aligned parallel to the Pt–Fe axis [C(2)–N–C(1)–Fe 4.14°]. Compared to **6a**, the C(1)–N–C(2) angle is somewhat widened and amounts to 127.2(9)°. At present we cannot state, whether this widening is due to a substituent effect on the phenyl group or caused by packing effects. The two mean planes defined by Fe–P(1)–P(2)–Pt and Fe–C(1)–Pt are nearly coplanar,

the angle between them being  $6.20^\circ$ . The rms deviation from the mean plane passing through Pt, C(1), P(2), P(3), and Fe is quite small and has been determined to be  $0.025 \text{ \AA}$  ( $0.051 \text{ \AA}$  for **6a**). As in **6a**, a distorted square planar description seems to be appropriate for the coordination geometry around the platinum center.

In order to obtain compounds **6a–c** in satisfactory yields (ca 65–75%), slow stoichiometric addition of the corresponding isonitrile is important. When **1a** was directly mixed with a stoichiometric quantity of CNR, the isolation of pure **6** was hampered by competing formation of the bis(isonitrile) complexes  $[(OC)_2(RN \equiv C)Fe(\mu-C \equiv N-R)(\mu-dppm)Pt(PPh_3)]$  (**7a**: R = 2,6-xylyl; **7b**: R = *p*-anisyl) and separation from unchanged starting material **1a**. Compounds **7**, possessing both a bridging and a terminal iron-bonded CNR ligand, were formed as the sole species, when **1a** was allowed to react with 2 equivalents of the corresponding isonitrile for 8 h at ambient temperature. The coordination of the terminal CNR ligand in an orthogonal position relative to the metal–metal bond can be deduced from the IR spectra, which showed two  $\nu(CO)$  stretches of approximate equal intensities. This pattern is only consistent with a *cis* arrangement of the two carbonyl ligands of the  $Fe(CO)_2$  unit.<sup>[22]</sup> In addition, two  $\nu(CN)$  vibrations due to the terminal and bridging isonitrile ligands were found in the IR spectra of **7a** and **7b** at 2089/2092 and 1655/1653  $cm^{-1}$ , respectively. Compared to complexes **6**, the position of the latter absorption is shifted by ca. 16 wavenumbers to lower frequencies. This is probably due to the additional electron-donating effect of the second terminal CNR ligand, which is partially compensated by back-bonding in  $\pi^*$  orbitals of the  $\mu$ -CNR ligand, thus weakening the C=N bond.

At first glance, the formation of **6** and **7** seems to involve a simple reductive elimination of  $HSi(OMe)_3$  as encountered in the  $\sigma$ -alkenyl– $\mu$ -vinylidene conversion of **2** into **4**. However, no evidence for the formation of trimethoxy silane was obtained. IR and  $^{31}P$ -NMR monitoring revealed that one hour after the addition of two equivalents of CNR, breaking of the metal–metal bond occurred. A doublet of doublets found in the  $^{31}P$ -NMR spectrum and an intense  $\nu(CO)$  stretch at  $1828 \text{ cm}^{-1}$  indicated the formation of the metallate  $[(OC)_3Fe\{Si(OMe)_3\}(\eta^1-dppm)]^-$ .<sup>[6]</sup> The nature of the cationic fragment remains speculative. The observation of a very broad resonance in the  $^{31}P$ -NMR spectrum at  $\delta = 13.1$  and a terminal  $\nu(CN)$  stretch at  $2185 \text{ cm}^{-1}$  could be consistent with the existence of cationic species of the type  $[Pt(H)(CNR)_2(PPh_3)]^+$ , similar to the known complexes *trans*- $[Pt(H)(CNp\text{-tol})(PEt_3)_2]^+$ ,  $[Pt(H)(CNp\text{-anisyl})(PEt_3)_2]^+$ , and  $[Pt(H)(PPh_3)_3]^+$ .<sup>[3a,23]</sup> This assumption is further corroborated by the observation of a new broad and unresolved hydride resonance in the  $^1H$ -NMR spectrum at  $\delta = -6.27$  exhibiting a Pt–H coupling constant of  $^1J = 804 \text{ Hz}$ . The mechanism of this reaction affording the  $\mu$ -isonitrile complexes **6** and **7** has not been investigated further, since in the meantime more rational syntheses for complexes  $[(OC)_3Fe(\mu-C \equiv N-R)(\mu-Ph_2PXPPH_2)Pt(PPh_3)]$  have been developed by us.<sup>[17b–17d]</sup>

### *N*-Protonation of $[(OC)_3Fe(\mu-CNR)(\mu-dppm)Pt(PPh_3)]$

As already described for  $[(OC)_3Fe(\mu-CNR)(\mu-dppa)Pt(PPh_3)]$ ,<sup>[17c,17d]</sup> electrophilic addition of  $H^+$  to the basic nitrogen atom of the  $\mu$ -(CNR) ligand of **6** led instantaneously in a quantitative manner to stable cationic  $\mu$ -aminocarbyne complexes  $[(OC)_3Fe(\mu-CN(H)R)(\mu-dppm)Pt(PPh_3)][BF_4]$  (**8a**: R = 2,6-xylyl; **8b**: R = *p*-anisyl; **8c**: R = *p*- $C_6H_4NH_2$ ) (Scheme 5). According to the  $FAB^+$  mass spectrum of the *p*- $C_6H_4NH_2$ -substituted derivative **8c**, which displayed an intense peak at  $m/z$  1100 (55%) for the cation, only monoprotection occurred, despite the use of excess  $HBF_4 \cdot Et_2O$ . Characteristic NMR features of these *N*-protonated species are given for **8a** as an example. In the  $^{13}C\{^1H\}$ -NMR spectrum, the resonance of the  $\mu$ -carbyne carbon is found downfield (doublet of doublets at  $\delta = 313.7$  with P–C couplings of  $^2J = 77$  and  $11 \text{ Hz}$ ; in the  $^1H$ -NMR spectrum, the N–H signal gave rise to a broad unresolved multiplet at  $\delta = 9.18$ . Compared to the neutral precursors **6a**, the  $P^1$ – $P^2$  coupling in the  $^{31}P\{^1H\}$ -NMR spectrum was substantially reduced to  $^{2+3}J = 89 \text{ Hz}$ . Furthermore, a up-field shift of the dppm resonances of ca. 14 ppm results from the *N*-protonation, whereas the position of the  $PPh_3$  ligand remains nearly unchanged. The doublet of doublets of doublets pattern at  $\delta = -2456$  observed in the  $^{195}Pt$ -NMR spectrum of **8a** is shifted downfield relative to the signal of **6a** ( $-2586$ ), the Pt–P<sup>3</sup> coupling constant being reduced from  $^1J = 4264 \text{ Hz}$  (**6a**) to  $^1J = 3739 \text{ Hz}$ . The similar  $^{31}P\{^1H\}$ -NMR spectrum of derivative **8b**, showing the three mutually coupled phosphorus nuclei together with the coupling to the  $^{195}Pt$  nucleus (33% natural abundance), is depicted in Figure 4.

A consequence of the positive charge, combined with the strong  $\pi$ -acceptor capacity of the  $\mu$ -aminoarbyne ligand, is the IR shift of the  $\nu(CO)$  vibrations to higher frequencies. Due to the decrease of the bond order of the C–N bond, the  $\nu(CN)$  absorption is now detected at  $1527 \text{ cm}^{-1}$ . These spectroscopic data indicate that the aminocarbyne complexes **8** are also structurally closely related to the  $\mu$ -vinylidene complexes **4** presented above.

### Conclusion

These investigations have shown that the alkoxysilyl-substituted dinuclear hydride complexes **1** possess an interesting reactivity towards unsaturated molecules, which in most cases is difficult to predict. Whereas 1-alkynes insert in a regioselective manner into the Pt–H bond of **1** to yield  $\sigma$ -alkenyl complexes, reaction with aromatic isonitriles affords the RNC-bridged Fe–Pt complexes **6** and **7**. The phosphane-induced  $\sigma$ -alkenyl– $\mu$ -vinylidene rearrangement leading to  $[(OC)_3Fe(\mu-C \equiv C(H)R)(\mu-Ph_2PXPPH_2)Pt(PR_3)]$  and the formation of the  $\mu$ -isonitrile complexes  $[(OC)_3Fe(\mu-C \equiv N-R)(\mu-dppm)Pt(PPh_3)]$  complement our previous studies on phosphane- and CO-induced silyl migrations resulting in  $\mu$ -silyloxycarbene complexes  $[(OC)_3Fe\{\mu-C(R)OSi(OMe)_3\}(\mu-dppm)Pt(PR_3)]$  and  $[(OC)_3Fe\{\mu-C(Me)OSi-$

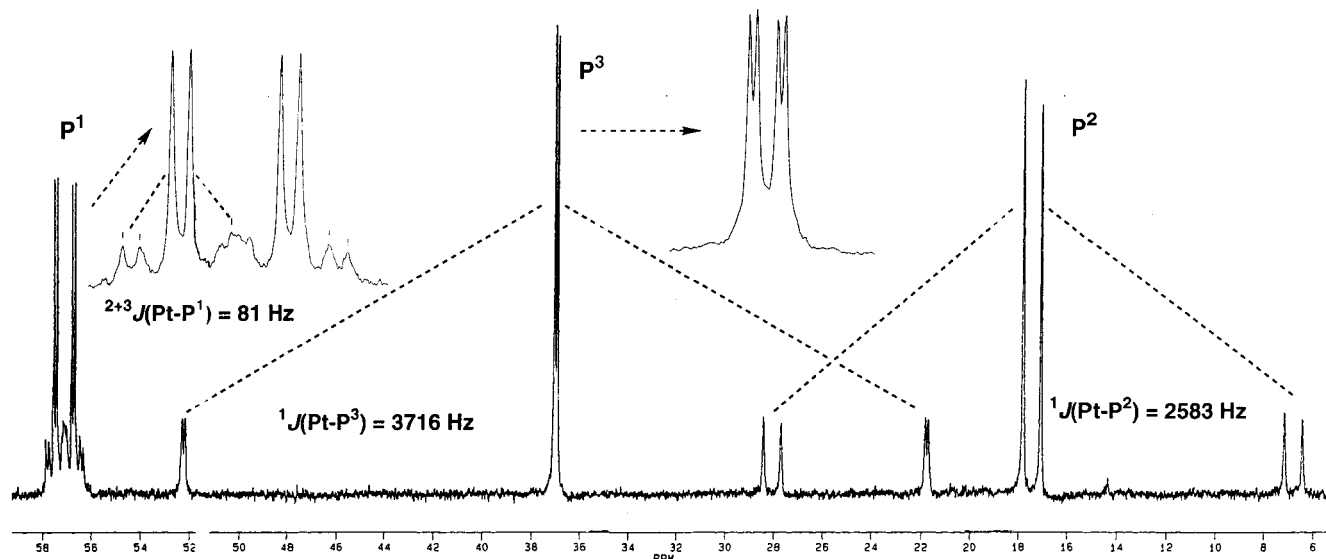


Figure 4.  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of  $[(\text{OC})_3\text{Fe}(\mu\text{-CN}(\text{H})p\text{-anisyl})(\mu\text{-dppm})\text{Pt}(\text{PPh}_3)][\text{BF}_4]$  **8b** showing the three mutually coupled phosphorus nuclei together with the  $^{195}\text{Pt}$  couplings

$(\text{OSiMe})_3\{\mu\text{-dppm}\}\text{Pd}(\text{CO})$ ].<sup>[12]</sup> The formation of these structurally closely related heterobimetallics underlines the tendency of these electron-rich systems to adopt a  $\text{Fe}(\mu\text{-C})\text{M}$  ( $\text{M} = \text{Pd}, \text{Pt}$ ) core structure, bridged by  $\mu$ -vinylidene,  $\mu$ -isonitrile,  $\mu$ -aminocarbene, and  $\mu$ -silyloxycarbene units behaving as efficient  $\pi$ -acceptor ligands. Our findings concerning the migratory insertion of activated alkynes such as DMAD or hexafluorobutyne into the  $\text{Pt-H}$  bond of **1**, as well as the molecular structures of the insertion products and their chemistry will be the subject of a forthcoming paper.<sup>[17c]</sup>

## Experimental Section

All reactions were performed in Schlenk-tube flasks under purified nitrogen. Solvents were dried and distilled under nitrogen before use, toluene and hexane from sodium, dichloromethane from  $\text{P}_4\text{O}_{10}$ . Nitrogen was passed through BASF R3-11 catalyst and molecular sieve columns to remove residual oxygen and water. – Elemental C, H, and N analyses were performed on a Leco Elemental Analyzer CHN 900. – The  $^1\text{H}$ -,  $^{31}\text{P}\{^1\text{H}\}$ -,  $^{29}\text{Si}$ -INEPT and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were recorded at 200.13, 81.01, 39.76, and 50.32 MHz, respectively, on a Bruker ACP 200 instrument. Phosphorus chemical shifts were referenced to 85%  $\text{H}_3\text{PO}_4$  in  $\text{H}_2\text{O}$  with downfield shifts reported as positive.  $^{195}\text{Pt}$  chemical shifts were measured with a Bruker ACP 200 instrument (42.95 MHz) and externally referenced to  $\text{K}_2\text{PtCl}_4$  in water with downfield chemical shifts reported as positive. NMR spectra were recorded in pure  $\text{CDCl}_3$ , unless otherwise stated. The presence and amount of  $\text{CH}_2\text{Cl}_2$  and  $\text{Et}_2\text{O}$  retained in **3a**, **3c**, **6a**, **8a**, and **8b** was determined from the  $^1\text{H}$ -NMR spectra. – The reactions were generally monitored by IR spectroscopy in the  $\nu(\text{CO})$  region. – The acetylenes and 2,6-xylyl isocyanide were obtained from Aldrich and Fluka and were used as received.  $[\text{Pt}(\text{Cl})(\text{H})(\text{PPh}_3)_2]$ ,  $[\text{Pt}(\text{H}_2\text{C}=\text{CH}_2)(\text{PPh}_3)_2]$ , dppa, dppm, and anisyl isocyanide were prepared as described in the literature.<sup>[24–28]</sup>  $[(\text{OC})_3\text{Fe}(\text{H})\{\text{Si}(\text{OMe})_3\}(\eta^1\text{-dppa})]$  was prepared as described for  $[(\text{OC})_3\text{Fe}(\text{H})\{\text{Si}(\text{OMe})_3\}(\eta^1\text{-dppm})]$ .<sup>[6]</sup>

**Preparation of  $[(\text{OC})_3\text{Fe}\{\text{Si}(\text{OMe})_3\}(\mu\text{-dppm})\text{Pt}(\text{H})(\text{PPh}_3)]$  (**1a**):** To a solution of  $[\text{Pt}(\text{H})(\text{Cl})(\text{PPh}_3)_2]$  (756 mg, 1.0 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL), 1 equiv. of  $\text{K}[(\text{OC})_3\text{Fe}\{\text{Si}(\text{OMe})_3\}(\eta^1\text{-dppm})]$  (685 mg, 1.0 mmol) was added. After stirring for 4 h at ambient temperature, the yellowish solution was filtered and concentrated. Compound **1a** was precipitated by slow addition of hexane and washed with  $\text{Et}_2\text{O}$ . The resulting crude off-white product, which was sufficiently pure for further reactions, was then dried in vacuo. Yield: 949 mg (86%). For  $^1\text{H}$ - and  $^{31}\text{P}$ -NMR data see ref.<sup>[5]</sup> – IR (KBr):  $\tilde{\nu} = 2149 \text{ cm}^{-1}$  (w)  $\nu(\text{PtH})$ ; 1952 (s), 1885 (vs), 1865 (vs)  $\nu(\text{CO})$ . –  $^{195}\text{Pt}\{^1\text{H}\}$  NMR:  $\delta = -2916$  [ddd,  $^{2+3}J(\text{Pt-P}^1) = 87$ ,  $^1J(\text{Pt-P}^2) = 2074$ ,  $^1J(\text{Pt-P}^3) = 3544$  Hz]. –  $^{29}\text{Si}$ -INEPT NMR:  $\delta = 10.6$  [dt,  $^3J(\text{P}^2\text{-Si}) = 7$ ,  $^3J(\text{P}^3\text{-Si}) = 7$ ,  $^2J(\text{P}^1\text{-Si}) = 38$  Hz]. –  $\text{C}_{49}\text{H}_{48}\text{FeO}_6\text{P}_3\text{PtSi}$  (1104.84): calcd. C 53.27, H 4.38; found C 52.50, H 4.09.

**Preparation of  $[(\text{OC})_3\text{Fe}\{\text{Si}(\text{OMe})_3\}(\mu\text{-dppa})\text{Pt}(\text{H})(\text{PPh}_3)]$  (**1b**):** To a solution of  $[\text{Pt}(\text{H}_2\text{C}=\text{CH}_2)(\text{PPh}_3)_2]$  (748 mg, 1.0 mmol) in toluene (10 mL), 1 equiv. of  $[(\text{OC})_3\text{Fe}(\text{H})\{\text{Si}(\text{OMe})_3\}(\eta^1\text{-dppa})]$  (647 mg, 1.0 mmol) was added. After stirring for 30 min at ambient temperature, the orange-red solution was concentrated and **1b** was precipitated by slow addition of hexane and washed with  $\text{Et}_2\text{O}$ . The resulting crude off-white product, which was sufficiently pure for further reactions, was then dried in vacuo. Yield: 905 mg (82%). Analytically pure **1b** was obtained in the form of colorless crystals by recrystallization from  $\text{CH}_2\text{Cl}_2$ /hexane. – IR (KBr):  $\tilde{\nu} = 2119 \text{ cm}^{-1}$  (w)  $\nu(\text{PtH})$ ; 1961 (s), 1896 (vs), 1887 (vs)  $\nu(\text{CO})$ . –  $^1\text{H}$  NMR:  $\delta = -4.09$  [dt, 1 H, PtH,  $^2J(\text{P}_{\text{trans}}\text{-H}) = 209$ ,  $^2J(\text{P}_{\text{cis}}\text{-H}) \approx ^3J(\text{P-H}) = 16$ ,  $^1J(\text{Pt-H}) = 662$  Hz], 3.58 [s, 9 H, SiOMe], 4.51 [m, br., NH,  $^3J(\text{Pt-H}) = 61.0$  Hz], 7.10–7.45 (m, 35 H, phenyl). –  $^{31}\text{P}\{^1\text{H}\}$  NMR:  $\delta = 119.7$  [dd,  $\text{P}^1(\text{Fe})$ ,  $^{2+3}J(\text{P}^1\text{-P}^2) = 138$ ,  $^{3+4}J(\text{P}^1\text{-P}^3) = 12$ ,  $^{2+3}J(\text{Pt-P}) = 87$  Hz], 81.7 [dd,  $\text{P}^2(\text{Pt})$ ,  $^1J(\text{Pt-P}) = 2284$  Hz], 29.9 [dd,  $\text{P}^3(\text{Pt})$ ,  $^2J(\text{P}^2\text{-P}^3) = 63$ ,  $^1J(\text{Pt-P}) = 3503$  Hz]. –  $^{195}\text{Pt}\{^1\text{H}\}$  NMR:  $\delta = -2999$  [ddd,  $^{2+3}J(\text{Pt-P}^1) = 87$ ,  $^1J(\text{Pt-P}^2) = 2884$ ,  $^1J(\text{Pt-P}^3) = 3503$  Hz]. –  $\text{C}_{48}\text{H}_{47}\text{FeNO}_6\text{P}_3\text{PtSi}$  (1104.80): calcd. C 52.18, H 4.28, N 1.27; found C 52.23, H 4.04, N 1.31.

**Preparation of  $[(\text{OC})_3\text{Fe}\{\text{Si}(\text{OMe})_3\}(\mu\text{-dppm})\text{Pt}(\text{H})(\text{PMePh}_2)]$  (**1c**):** To a solution of  $[\text{Pt}(\text{H}_2\text{C}=\text{CH}_2)(\text{PMePh}_2)_2]$  (624 mg, 1.0 mmol) in toluene (10 mL), 1 equiv. of  $[(\text{OC})_3\text{Fe}(\text{H})\{\text{Si}(\text{OMe})_3\}(\eta^1\text{-dppm})]$  (646 mg, 1.0 mmol) was added. After stirring for 30 min at ambient temperature, the orange-red solution was concentrated and **1c** was



precipitated by slow addition of hexane. The resulting crude off-white product, which was sufficiently pure for further reactions, was then dried in vacuo. Yield: 854 mg (82%). – IR (KBr):  $\tilde{\nu}$  = 2114  $\text{cm}^{-1}$  (w)  $\nu(\text{PtH})$ ; 1952 (s), 1880 (vs), 1860 (vs)  $\nu(\text{CO})$ . –  $^1\text{H}$  NMR:  $\delta$  = –4.23 [dt, 1 H, PtH,  $^2J(\text{P}_{\text{trans}}\text{-H})$  = 188,  $^2J(\text{P}_{\text{cis}}\text{-H}) \approx ^3J(\text{P-H})$  = 14,  $^1J(\text{Pt-H})$  = 693 Hz], 2.11 [d, 3 H,  $\text{PCH}_3$ ,  $^2J(\text{P-H})$  = 10 Hz], 3.46 [t, br., 2 H,  $\text{CH}_2$ ,  $^2J(\text{P-H})$  = 12 Hz], 3.63 [s, 9 H, SiOMe], 6.90–7.65 (m, 25 H, phenyl). –  $^{31}\text{P}\{^1\text{H}\}$  NMR:  $\delta$  = 70.2 [dd,  $\text{P}^1(\text{Fe})$ ,  $^{2+3}J(\text{P}^1\text{-P}^2)$  = 128,  $^{3+4}J(\text{P}^1\text{-P}^3)$  = 12,  $^{2+3}J(\text{Pt-P})$  = 84 Hz], 28.5 [dd,  $\text{P}^2(\text{Pt})$ ,  $^1J(\text{Pt-P})$  = 2068 Hz], 28.0 [t,  $\text{P}^3(\text{Pt})$ ,  $^2J(\text{P}^2\text{-P}^3)$  = 12,  $^1J(\text{Pt-P})$  = 3571 Hz]. –  $^{195}\text{Pt}\{^1\text{H}\}$  NMR:  $\delta$  = –2933 [ddd,  $^{2+3}J(\text{Pt-P}^1)$  = 84,  $^1J(\text{Pt-P}^2)$  = 2068,  $^1J(\text{Pt-P}^3)$  = 3571 Hz]. –  $\text{C}_{44}\text{H}_{45}\text{FeO}_6\text{P}_3\text{PtSi}$  (1041.78): calcd. C 50.73, H 4.35; found C 51.13, H 4.78.

**Preparation of  $[(\text{OC})_3\text{Fe}\{\mu\text{-Si}(\text{OMe})_2(\text{OMe})\}(\mu\text{-dppm})\text{Pt}\{\text{C}(\text{CO}_2\text{Me})=\text{CH}_2\}]$  (2a):** To a solution of **1a** (552 mg, 0.5 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL), 3 equiv. of methyl propiolate was added. After stirring for 4 h at ambient temperature, the orange-red solution was concentrated and **2a** was precipitated by slow addition of hexane. The resulting crude orange-yellow product, which was sufficiently pure for further reactions, was then dried in vacuo. Yield: 905 mg (79%). An analytically pure sample was obtained by recrystallization from toluene/pentane. – IR (KBr):  $\tilde{\nu}$  = 1971 (s), 1909 (vs), 1879 (s), 1687 (m)  $\nu(\text{CO})$ . –  $^1\text{H}$  NMR:  $\delta$  = 3.41 [s, 3 H,  $\text{CO}_2\text{Me}$ ], 3.65 [d, 3 H, Pt–OCH<sub>3</sub>,  $^4J(\text{Pt-H})$  = 2 Hz], 3.78 [s, 6 H, SiOCH<sub>3</sub> (PCH<sub>2</sub>P resonances obscured by the signals for the methoxy groups)], 5.08 [d, 1 H, (Z)-vinyl-H,  $^4J(\text{P-H})$  = 2 Hz,  $^3J(\text{Pt-H})$  = 62 Hz], 6.56 [s, 1 H, (E)-vinyl-H,  $^3J(\text{Pt-H})$  = 118 Hz], 7.17–7.92 (m, 20 H, phenyl). –  $^{13}\text{C}\{^1\text{H}\}$  NMR:  $\delta$  = 216.4 [d, 2 CO,  $^2J(\text{P-C})$  = 17 Hz], 212.4 [d, 1 CO,  $^2J(\text{P-C})$  = 13 Hz], 171.7 [s, C(=O)OCH<sub>3</sub>], 156.6 [d, C<sub>ar</sub>,  $^2J(\text{P-C})$  = 8 Hz], 120.3–138.2 (m, phenyl and C<sub>β</sub>), 55.1 (s, Pt–OCH<sub>3</sub>), 51.0 [s, C(=O)OCH<sub>3</sub>], 50.7 (s, SiOCH<sub>3</sub>), 45.4 [dd, PCP,  $^1J(\text{P-C})$  = 22,  $^1J(\text{P-C})$  = 39 Hz]. –  $^{31}\text{P}\{^1\text{H}\}$  NMR:  $\delta$  = 59.8 [d,  $\text{P}^1(\text{Fe})$ ,  $^{2+3}J(\text{P}^1\text{-P}^2)$  = 41,  $^{2+3}J(\text{Pt-P})$  = 61 Hz], 5.6 [d,  $\text{P}^2(\text{Pt})$ ,  $^1J(\text{Pt-P})$  = 5010 Hz]. –  $^{195}\text{Pt}\{^1\text{H}\}$  NMR:  $\delta$  = –2317 [dd,  $^{2+3}J(\text{Pt-P}^1)$  = 61,  $^1J(\text{Pt-P}^2)$  = 5010 Hz]. –  $^{29}\text{Si}$ -INEPT NMR:  $\delta$  = 17.0 [dd,  $^3J(\text{P}^2\text{-Si})$  = 5,  $^2J(\text{P}^1\text{-Si})$  = 35 Hz] –  $\text{C}_{35}\text{H}_{36}\text{FeO}_8\text{P}_2\text{PtSi} \cdot 0.25 \text{C}_7\text{H}_8$  (925.63 + 22.81): calcd. C 46.53, H 4.04; found C 46.58, H 3.70.

**Preparation of  $[(\text{OC})_3\text{Fe}\{\mu\text{-Si}(\text{OMe})_2(\text{OMe})\}(\mu\text{-dppa})\text{Pt}\{\text{C}(\text{CO}_2\text{Me})=\text{CH}_2\}]$  (2b):** This complex was prepared as described for **2a**. Yield: 678 mg (70%). An analytically pure sample of **2b** containing triphenylphosphane oxide (see text) was obtained in small amounts after two weeks at –25°C from a  $\text{CH}_2\text{Cl}_2$ /pentane mixture. – IR (KBr):  $\tilde{\nu}$  = 1975 (s), 1909 (vs), 1890 (s), 1687 (m)  $\nu(\text{CO})$ . –  $^1\text{H}$  NMR:  $\delta$  = 3.33 [s, 3 H,  $\text{CO}_2\text{Me}$ ], 3.69 [s, 3 H, Pt–OCH<sub>3</sub>], 3.75 [s, 6 H, SiOCH<sub>3</sub>], 4.79 [m, br., NH,  $^3J(\text{Pt-H})$  = 108 Hz], 5.33 [s, 1 H, (Z)-vinyl-H,  $^3J(\text{Pt-H})$  = 67 Hz], 6.82 [s, 1 H, (E)-vinyl-H,  $^3J(\text{Pt-H})$  = 122 Hz], 7.16–7.86 (m, 20 H, phenyl). –  $^{31}\text{P}\{^1\text{H}\}$  NMR:  $\delta$  = 109.5 [d,  $\text{P}^1(\text{Fe})$ ,  $^{2+3}J(\text{P}^1\text{-P}^2)$  = 45,  $^{2+3}J(\text{Pt-P})$  = 50 Hz], 44.7 [d,  $\text{P}^2(\text{Pt})$ ,  $^1J(\text{Pt-P})$  = 5299 Hz], 28.8 [s, OPPh<sub>3</sub>]. –  $^{195}\text{Pt}\{^1\text{H}\}$  NMR:  $\delta$  = –2350 [dd,  $^{2+3}J(\text{Pt-P}^1)$  = 50,  $^1J(\text{Pt-P}^2)$  = 5299 Hz]. –  $^{29}\text{Si}$ -INEPT NMR:  $\delta$  = 16.1 [dd,  $^3J(\text{P}^2\text{-Si})$  = 5,  $^2J(\text{P}^1\text{-Si})$  = 38 Hz]. –  $\text{C}_{34}\text{H}_{35}\text{FeNO}_8\text{P}_2\text{PtSi} \cdot \text{O}=\text{PPh}_3$  (1204.91): calcd. C 51.84, H 4.18, N 1.16; found C 50.36, H 3.96, N 1.29.

**Preparation of  $[(\text{OC})_3\text{Fe}\{\mu\text{-Si}(\text{OMe})_2(\text{OMe})\}(\mu\text{-dppm})\text{Pt}\{\text{C}(\text{Ph})=\text{CH}_2\}]$  (3a):** To a solution of **1a** (1105 mg, 1.0 mmol) in  $\text{CH}_2\text{Cl}_2$  (20 mL), 10 equivalents of phenylacetylene were added. After stirring for 5 h at ambient temperature, all volatiles were removed in vacuo. The oily red–brown residue was rinsed with 40 mL of a ether/hexane mixture (75:25) to extract **3a** from unchanged **1a** and **4a**. On concentration of the extract, crude **3a** pre-

cipitated as an ochre solid. Analytically pure **3a** was obtained by redissolving the solid in 3 mL of  $\text{CH}_2\text{Cl}_2$  and precipitation with cold pentane (15 mL). Yield: 158 mg (16%). – IR ( $\text{CH}_2\text{Cl}_2$ ):  $\tilde{\nu}$  = 1962 (s), 1999 (vs), 1870 (vs)  $\nu(\text{CO})$ ; 1588 (w)  $\nu(\text{C}=\text{C})$ . –  $^1\text{H}$  NMR:  $\delta$  = 3.54 [t, 2 H, PCH<sub>2</sub>P,  $^2J(\text{P-H})$  = 10.8 Hz], 3.65 [d, 3 H, Pt–OCH<sub>3</sub>,  $^4J(\text{Pt-H})$  = 2.4 Hz], 3.76 [s, 6 H, SiOCH<sub>3</sub>], 5.09 [s, 1 H, (Z)-vinyl-H,  $^3J(\text{Pt-H})$  = 58 Hz], 5.96 [s, 1 H, (E)-vinyl-H,  $^3J(\text{Pt-H})$  = 108 Hz], 6.86–7.67 (m, 25 H, phenyl). –  $^{13}\text{C}\{^1\text{H}\}$  NMR (268 K):  $\delta$  = 217.0 [d, 2 CO,  $^2J(\text{P-C})$  = 18 Hz], 212.7 [d, 1 CO,  $^2J(\text{P-C})$  = 13 Hz], 166.5 [dd, C<sub>ar</sub>,  $^2J(\text{P-C})$  = 6,  $^3J(\text{P-C})$  = 2 Hz], 120.3–138.2 (m, phenyl), 117.0 (s, br, C<sub>β</sub>), 54.8 (s, Pt–OCH<sub>3</sub>), 50.7 (s, SiOCH<sub>3</sub>), 44.6 [dd, PCP,  $^1J(\text{P-C})$  = 22,  $^1J(\text{P-C})$  = 39 Hz]. –  $^{31}\text{P}\{^1\text{H}\}$  NMR:  $\delta$  = 61.2 [d,  $\text{P}^1(\text{Fe})$ ,  $^{2+3}J(\text{P}^1\text{-P}^2)$  = 41,  $^{2+3}J(\text{Pt-P})$  = 60 Hz], 6.9 [d,  $\text{P}^2(\text{Pt})$ ,  $^1J(\text{Pt-P})$  = 5246 Hz]. –  $^{195}\text{Pt}\{^1\text{H}\}$  NMR:  $\delta$  = –2308 [dd,  $^{2+3}J(\text{Pt-P}^1)$  = 60,  $^1J(\text{Pt-P}^2)$  = 5246 Hz]. –  $^{29}\text{Si}$ -INEPT NMR:  $\delta$  = 17.9 [dd,  $^3J(\text{P}^2\text{-Si})$  = 4,  $^2J(\text{P}^1\text{-Si})$  = 34 Hz]. –  $\text{C}_{39}\text{H}_{38}\text{FeO}_6\text{P}_2\text{PtSi} \cdot 0.5 \text{CH}_2\text{Cl}_2$  (943.69 + 42.47): calcd. C 48.11, H 3.99; found C 48.46, H 4.08.

**Preparation of  $[(\text{OC})_3\text{Fe}\{\mu\text{-C}=\text{C}(\text{H})\text{Ph}\}(\mu\text{-dppa})\text{Pt}(\text{PPh}_3)]$  (4b):** To a solution of **1b** (551 mg, 0.5 mmol) in  $\text{CH}_2\text{Cl}_2$  (15 mL), 10 equiv. of phenylacetylene was added. After stirring for 2 d at 35°C, the color of the solution had changed to red–brown. All volatiles were removed in vacuo, the residue redissolved in  $\text{CH}_2\text{Cl}_2$  (5 mL) and layered with hexane (15 mL). After 3 d at 5°C, yellow microcrystals were formed. Yield: 367 mg (68%). – IR (KBr):  $\tilde{\nu}$  = 3295  $\nu(\text{NH})$ ; 2007 (m), 1942 (vs), 1916 (m)  $\nu(\text{CO})$ ; 1585 (w)  $\nu(\text{C}=\text{C})$ . –  $^1\text{H}$  NMR:  $\delta$  = 5.22 [m, br., NH,  $^3J(\text{Pt-H})$  = 89.0 Hz], 6.60–8.25 [m, 41 H, phenyl and vinylidene proton]. –  $^{13}\text{C}\{^1\text{H}\}$  NMR (263 K):  $\delta$  = 238.8 [dd,  $\mu\text{-C}_{ar}$ ,  $^2J(\text{P-C})$  = 72,  $^2J(\text{P-C})$  = 12 Hz], 217.3 [d, 1 CO,  $^2J(\text{P-C})$  = 6 Hz], 213.8 (dd, 2 CO,  $^2J(\text{P-C})$ ,  $^3J(\text{P-C})$  = 5 Hz], 117.9–138.4 [m, phenyl]. –  $^{31}\text{P}\{^1\text{H}\}$  NMR:  $\delta$  = 107.9 [dd,  $\text{P}^1(\text{Fe})$ ,  $^{2+3}J(\text{P}^1\text{-P}^2)$  = 132,  $^{3+4}J(\text{P}^1\text{-P}^3)$  = 14,  $^{2+3}J(\text{Pt-P})$  = 62 Hz], 80.4 [dd,  $\text{P}^2(\text{Pt})$ ,  $^1J(\text{Pt-P})$  = 2778 Hz], 42.7 [dd,  $\text{P}^3(\text{Pt})$ ,  $^2J(\text{P}^2\text{-P}^3)$  = 33,  $^1J(\text{Pt-P})$  = 4101 Hz]. –  $^{195}\text{Pt}\{^1\text{H}\}$  NMR:  $\delta$  = –2308 [ddd,  $^{2+3}J(\text{Pt-P}^1)$  = 62,  $^1J(\text{Pt-P}^2)$  = 2777,  $^1J(\text{Pt-P}^3)$  = 4101 Hz]. –  $\text{C}_{53}\text{H}_{42}\text{FeNO}_3\text{P}_3\text{Pt}$  (1084.78): calcd. C 58.68, H 3.90, N 1.29; found C 58.29, H 3.61, N 1.20.

**Preparation of  $[(\text{OC})_3\text{Fe}\{\mu\text{-C}=\text{C}(\text{H})\text{Ph}\}(\mu\text{-dppm})\text{Pt}(\text{PMePh}_2)]$  (4c):** This complex was prepared in an NMR tube experiment by addition of excess phenylacetylene to a solution of **1c** (26 mg, 0.025 mmol) in  $\text{CDCl}_3$  (0.7 mL) and was only characterized spectroscopically. – IR (KBr):  $\tilde{\nu}$  = 1990 (m), 1925 (vs), 1904 (s)  $\nu(\text{CO})$ ; 1592 (w)  $\nu(\text{C}=\text{C})$ . –  $^{31}\text{P}\{^1\text{H}\}$  NMR:  $\delta$  = 62.2 [dd,  $\text{P}^1(\text{Fe})$ ,  $^{2+3}J(\text{P}^1\text{-P}^2)$  = 116,  $^{3+4}J(\text{P}^1\text{-P}^3)$  = 14,  $^{2+3}J(\text{Pt-P})$  = 78 Hz], 40.9 [t,  $\text{P}^3(\text{Pt})$ ,  $^2J(\text{P}^2\text{-P}^3)$  = 15,  $^1J(\text{Pt-P})$  = 4056 Hz], 21.4 [dd,  $\text{P}^2(\text{Pt})$ ,  $^1J(\text{Pt-P})$  = 2462 Hz].

**Preparation of  $[(\text{OC})_3\text{Fe}\{\mu\text{-C}=\text{C}(\text{H})\text{-}p\text{-tol}\}(\mu\text{-dppm})\text{Pt}(\text{PPh}_3)]$  (4d):** This complex was prepared as described for **4b** by mixing **1a** (551 mg, 0.5 mmol) in  $\text{CH}_2\text{Cl}_2$  (15 mL) with 8 equiv. of *p*-tolylacetylene. Yield: 374 mg (61%). – IR (KBr):  $\tilde{\nu}$  = 1987 (m), 1921 (vs), 1903 (s)  $\nu(\text{CO})$ ; 1581 (w)  $\nu(\text{C}=\text{C})$ . –  $^1\text{H}$  NMR:  $\delta$  = 2.26 [s, 3 H, tolyl-CH<sub>3</sub>], 4.03 [t, br., 2 H,  $\text{CH}_2$ ,  $^2J(\text{P-H})$  = 9.8,  $^3J(\text{Pt-H})$  = 38.3 Hz], 6.58–7.0 [m, 40 H, phenyl and vinylidene proton]. –  $^{31}\text{P}\{^1\text{H}\}$  NMR:  $\delta$  = 62.9 [dd,  $\text{P}^1(\text{Fe})$ ,  $^{2+3}J(\text{P}^1\text{-P}^2)$  = 117,  $^{3+4}J(\text{P}^1\text{-P}^3)$  = 15,  $^{2+3}J(\text{Pt-P})$  = 79 Hz], 43.3 [dd,  $\text{P}^3(\text{Pt})$ ,  $^2J(\text{P}^2\text{-P}^3)$  = 19,  $^1J(\text{Pt-P})$  = 4023 Hz], 21.8 [dd,  $\text{P}^2(\text{Pt})$ ,  $^1J(\text{Pt-P})$  = 2477 Hz]. –  $^{195}\text{Pt}\{^1\text{H}\}$  NMR:  $\delta$  = –2703 [ddd,  $^{2+3}J(\text{Pt-P}^1)$  = 79,  $^1J(\text{Pt-P}^2)$  = 2477,  $^1J(\text{Pt-P}^3)$  = 4023 Hz]. –  $\text{C}_{55}\text{H}_{45}\text{FeO}_3\text{P}_3\text{Pt} \cdot 1.5 \text{CH}_2\text{Cl}_2$  (1097.81 + 127.40): calcd. C 55.39, H 3.95; found C 55.13, H 4.16.

**Preparation of  $[(\text{OC})_3\text{Fe}\{\text{Si}(\text{OMe})_3\}(\mu\text{-dppm})\text{Pt}(\text{CN-2,6-xylyl})\{\text{C}(\text{CO}_2\text{Me})=\text{CH}_2\}]$  (5b):** 2,6-Xylyl isocyanide (26 mg, 0.2 mmol) was added to a stirred solution of **2a** (190 mg, 0.2 mmol) in  $\text{CH}_2\text{Cl}_2$

(7 mL). The orange–red solution was stirred for 10 min at ambient temperature, then the volume was reduced to ca. 2 mL. After addition of pentane, the product precipitated in the form of an orange–red solid. Yield: 199 mg (94%). – IR (KBr):  $\tilde{\nu}$  = 2181 (s)  $\nu(\text{C}\equiv\text{N})$ ; 1959 (s), 1892 (vs), 1865 (vs), 1691 (m)  $\nu(\text{CO})$ . –  $^1\text{H}$  NMR:  $\delta$  = 2.45 [s, 6 H, xylyl- $\text{CH}_3$ ], 3.29 [s, 3 H,  $\text{CO}_2\text{Me}$ ], 3.59 [s, 9 H,  $\text{SiOCH}_3$  (PCH<sub>2</sub>P resonances obscured by the methoxy groups)], 5.27 [s, 1 H, (Z)-vinyl-H,  $^3J(\text{Pt-H})$  = 80 Hz], 6.79 [s, 1 H, (E)-vinyl-H,  $^3J(\text{Pt-H})$  = 142 Hz], 7.03–7.87 (m, 23 H, phenyl). –  $^{31}\text{P}\{^1\text{H}\}$  NMR:  $\delta$  = 62.9 [d,  $\text{P}^1(\text{Fe})$ ,  $^{2+3}J(\text{P}^1\text{-P}^2)$  = 84,  $^{2+3}J(\text{Pt-P})$  = 38 Hz], 13.4 [d,  $\text{P}^2(\text{Pt})$ ,  $^1J(\text{Pt-P})$  = 3182 Hz]. –  $^{195}\text{Pt}\{^1\text{H}\}$  NMR:  $\delta$  = –2698 [d, br,  $^{2+3}J(\text{Pt-P}^1)$  not resolved,  $^1J(\text{Pt-P}^2)$  = 3182 Hz]. –  $\text{C}_{44}\text{H}_{45}\text{FeNO}_8\text{P}_2\text{PtSi}$  (1056.81): calcd. C 50.01, H 4.29, N 1.32; found C 50.48, H 4.68, N 1.10.

**Preparation of [(OC)<sub>3</sub>Fe(Si(OMe)<sub>3</sub>)(μ-dppm)Pt(CN–2,6-xylyl)-C(Ph)=CH<sub>2</sub>)] (5c):** 2,6-Xylyl isocyanide (13 mg, 0.1 mmol) was added to a stirred solution of **3a** (99 mg, 0.1 mmol) in  $\text{CH}_2\text{Cl}_2$  (5 mL). The orange–red solution was stirred for 10 min at ambient temperature, then the volume was reduced to ca. 2 mL. After addition of pentane, the product precipitated in the form of an orange–red solid, which was dried in vacuo for 2 h. Yield: 76 mg (71%). – IR (KBr):  $\tilde{\nu}$  = 2176 (s)  $\nu(\text{C}\equiv\text{N})$ ; 1955 (s), 1889 (vs), 1858 (vs)  $\nu(\text{CO})$ . –  $^1\text{H}$  NMR:  $\delta$  = 2.34 [s, 6 H, xylyl- $\text{CH}_3$ ], 3.50 [m, 1 H, PCH<sub>2</sub>P], 3.57 [s, 9 H,  $\text{SiOCH}_3$ ], 3.80 [m, 1 H, PCH<sub>2</sub>P], 5.08 [s, 1 H, (Z)-vinyl-H,  $^3J(\text{Pt-H})$  = 77 Hz], 6.16 [s, 1 H, (E)-vinyl-H,  $^3J(\text{Pt-H})$  = 141 Hz], 6.89–7.69 (m, 28 H, phenyl). –  $^{31}\text{P}\{^1\text{H}\}$  NMR:  $\delta$  = 63.5 [d,  $\text{P}^1(\text{Fe})$ ,  $^{2+3}J(\text{P}^1\text{-P}^2)$  = 87,  $^{2+3}J(\text{Pt-P})$  = 34 Hz], 14.0 [d,  $\text{P}^2(\text{Pt})$ ,  $^1J(\text{Pt-P})$  = 3313 Hz]. –  $\text{C}_{48}\text{H}_{47}\text{FeNO}_6\text{P}_2\text{PtSi}$  (1074.81): calcd. C 53.64, H 4.41, N 1.30; found C 53.37, H 4.10, N 1.12.

**Preparation of [(OC)<sub>3</sub>Fe(μ-C≡N–xylyl)(μ-dppm)Pt(PPh<sub>3</sub>)] (6a):** 2,6-Xylyl isocyanide (131 mg, 1 mmol) was added in several portions over 30 min to a stirred solution of **1a** (1105 mg, 1.0 mmol) in  $\text{CH}_2\text{Cl}_2$  (20 mL). The orange–red solution was stirred for 1 d at ambient temperature, then reduced to ca. 5 mL and layered with Et<sub>2</sub>O. After 3 d at 5° C, orange crystals of **6a** containing 1.5 molecules of solvated  $\text{CH}_2\text{Cl}_2$  were formed. These crystals rapidly lost 0.5 molecules of solvated  $\text{CH}_2\text{Cl}_2$  in vacuo. Yield: 910 mg (76%). – IR ( $\text{CH}_2\text{Cl}_2$ ):  $\tilde{\nu}$  = 1994 (m), 1926 (vs),  $\nu(\text{CO})$ ; 1667 (m, br)  $\nu(\text{C}\equiv\text{N})$ . –  $^1\text{H}$  NMR:  $\delta$  = 2.18 [s, 6 H, xylyl- $\text{CH}_3$ ], 3.69 [t, 2 H,  $\text{CH}_2$ ,  $^2J(\text{P-H})$  = 9.0,  $^3J(\text{Pt-H})$  = 37.0 Hz], 6.83–7.48 [m, 38 H, phenyl]. –  $^{31}\text{P}\{^1\text{H}\}$  NMR:  $\delta$  = 73.6 [dd,  $\text{P}^1(\text{Fe})$ ,  $^{2+3}J(\text{P}^1\text{-P}^2)$  = 152,  $^{3+4}J(\text{P}^1\text{-P}^3)$  = 5,  $^{2+3}J(\text{Pt-P})$  = 75 Hz], 42.0 [dd,  $\text{P}^3(\text{Pt})$ ,  $^2J(\text{P}^2\text{-P}^3)$  = 27,  $^1J(\text{Pt-P})$  = 4264 Hz], 32.7 [dd,  $\text{P}^2(\text{Pt})$ ,  $^1J(\text{Pt-P})$  = 2527 Hz]. –  $^{195}\text{Pt}\{^1\text{H}\}$  NMR:  $\delta$  = –2586 [ddd,  $^{2+3}J(\text{Pt-P}^1)$  = 75,  $^1J(\text{Pt-P}^2)$  = 2527,  $^1J(\text{Pt-P}^3)$  = 4264 Hz]. –  $\text{C}_{55}\text{H}_{46}\text{FeNO}_3\text{P}_3\text{Pt} \cdot \text{CH}_2\text{Cl}_2$  (1112.83 + 84.93): calcd. C 56.15, H 4.04, N 1.17; found C 55.70, H 4.08, N 1.14.

**Preparation of [(OC)<sub>3</sub>Fe(μ-C≡N–o-anisyl)(μ-dppm)Pt(PPh<sub>3</sub>)] (6b):** This complex was prepared as described for **6a** by adding *o*-anisyl isocyanide (133 mg, 1 mmol) (dissolved in 5 mL  $\text{CH}_2\text{Cl}_2$ ) dropwise to a solution of **1a** (1105 mg, 1 mmol) in  $\text{CH}_2\text{Cl}_2$  (15 mL). Yield: 825 mg (74%). – IR ( $\text{CH}_2\text{Cl}_2$ ):  $\tilde{\nu}$  = 1998 (m), 1929 (vs)  $\nu(\text{CO})$ ; 1668 (m, br)  $\nu(\text{C}\equiv\text{N})$ . –  $^1\text{H}$  NMR:  $\delta$  = 3.86 [s, 3 H,  $\text{OCH}_3$ ], 3.88–4.00 [ $\text{CH}_2$ , partially hidden by the methoxy resonance], 6.80–7.58 [m, 39 H, phenyl]. –  $^{31}\text{P}\{^1\text{H}\}$  NMR:  $\delta$  = 73.6 [dd,  $\text{P}^1(\text{Fe})$ ,  $^{2+3}J(\text{P}^1\text{-P}^2)$  = 152,  $^{3+4}J(\text{P}^1\text{-P}^3)$  = 5,  $^{2+3}J(\text{Pt-P})$  = 69 Hz], 42.0 [dd,  $\text{P}^3(\text{Pt})$ ,  $^2J(\text{P}^2\text{-P}^3)$  = 27,  $^1J(\text{Pt-P})$  = 4188 Hz], 30.2 [dd,  $\text{P}^2(\text{Pt})$ ,  $^1J(\text{Pt-P})$  = 2527 Hz]. –  $^{195}\text{Pt}\{^1\text{H}\}$  NMR:  $\delta$  = –2594 [ddd,  $^{2+3}J(\text{Pt-P}^1)$  = 69,  $^1J(\text{Pt-P}^2)$  = 2527,  $^1J(\text{Pt-P}^3)$  = 4188 Hz]. –  $\text{C}_{54}\text{H}_{44}\text{FeNO}_4\text{P}_3\text{Pt}$  (1114.81): calcd. C 58.18, H 3.99, N 1.26; found C 58.00, H 3.81, N 1.14.

**Preparation of [(OC)<sub>3</sub>Fe(μ-C≡N–*p*-anisyl)(μ-dppm)Pt(PPh<sub>3</sub>)] (6c):** This complex was prepared as described for **6a** by adding *p*-anisyl isocyanide (133 mg, 1 mmol) (dissolved in 5 mL  $\text{CH}_2\text{Cl}_2$ ) dropwise to a solution of **1a** (1105 mg, 1 mmol) in  $\text{CH}_2\text{Cl}_2$  (15 mL). Yield: 825 mg (74%). – IR ( $\text{CH}_2\text{Cl}_2$ ):  $\tilde{\nu}$  = 1996 (m), 1928 (vs)  $\nu(\text{CO})$ ; 1669 (m, br)  $\nu(\text{C}\equiv\text{N})$ . –  $^1\text{H}$  NMR:  $\delta$  = 3.81 [s, 3 H,  $\text{OCH}_3$ ], 3.79 [t, 2 H,  $\text{CH}_2$ ,  $^2J(\text{P-H})$  = 10.0,  $^3J(\text{Pt-H})$  = 39.0 Hz] 6.57–7.77 [m, 39 H, phenyl]. –  $^{31}\text{P}\{^1\text{H}\}$  NMR:  $\delta$  = 71.2 [dd,  $\text{P}^1(\text{Fe})$ ,  $^{2+3}J(\text{P}^1\text{-P}^2)$  = 153,  $^{3+4}J(\text{P}^1\text{-P}^3)$  = 4,  $^{2+3}J(\text{Pt-P})$  = 67 Hz], 41.7 [dd,  $\text{P}^3(\text{Pt})$ ,  $^2J(\text{P}^2\text{-P}^3)$  = 29,  $^1J(\text{Pt-P})$  = 4196 Hz], 30.2 [dd,  $\text{P}^2(\text{Pt})$ ,  $^1J(\text{Pt-P})$  = 2490 Hz]. –  $\text{C}_{54}\text{H}_{44}\text{FeNO}_4\text{P}_3\text{Pt}$  (1114.81): calcd. C 58.18, H 3.99, N 1.26; found C 58.09, H 4.35, N 1.47.

**Preparation of [(OC)<sub>3</sub>Fe(μ-C≡N–*p*-C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>)(μ-dppm)Pt(PPh<sub>3</sub>)] (6d):** This complex was prepared as described for **6a** by adding *p*-aminophenyl isocyanide (118 mg, 1 mmol) (dissolved in 5 mL  $\text{CH}_2\text{Cl}_2$ ) dropwise to a solution of **1a** (1105 mg, 1 mmol) in  $\text{CH}_2\text{Cl}_2$  (15 mL). Yield: 715 mg (65%). – IR ( $\text{CH}_2\text{Cl}_2$ ):  $\tilde{\nu}$  = 1995 (m), 1927 (vs)  $\nu(\text{CO})$ ; 1668 (m, br)  $\nu(\text{C}\equiv\text{N})$ . –  $^1\text{H}$  NMR:  $\delta$  = 3.421 [s, br, 2 H,  $\text{NH}_2$ ], 3.80 [t,  $\text{CH}_2$ ,  $^2J(\text{P-H})$  = 9.8,  $^3J(\text{Pt-H})$  = 40.0 Hz], 6.78–7.72 [m, 39 H, phenyl]. –  $^{31}\text{P}\{^1\text{H}\}$  NMR:  $\delta$  = 71.3 [dd,  $\text{P}^1(\text{Fe})$ ,  $^{2+3}J(\text{P}^1\text{-P}^2)$  = 154,  $^{3+4}J(\text{P}^1\text{-P}^3)$  = 4,  $^{2+3}J(\text{Pt-P})$  = 66 Hz], 42.0 [dd,  $\text{P}^3(\text{Pt})$ ,  $^2J(\text{P}^2\text{-P}^3)$  = 29,  $^1J(\text{Pt-P})$  = 4012 Hz], 30.3 [dd,  $\text{P}^2(\text{Pt})$ ,  $^1J(\text{Pt-P})$  = 2556 Hz]. –  $\text{C}_{53}\text{H}_{43}\text{FeN}_2\text{O}_3\text{P}_3\text{Pt}$  (1099.79): calcd. C 57.88, H 3.94, N 2.55; found C 57.90, H 4.21, N 2.47.

**Preparation of [(OC)<sub>2</sub>(xylylNC)Fe(μ-C≡N–xylyl)(μ-dppm)Pt(PPh<sub>3</sub>)] (7a):** 2,6-Xylyl isocyanide (131 mg, 1 mmol) was added to a stirred solution of **1a** (552 mg, 0.5 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL). The orange–red solution was stirred for 8 h at ambient temperature, then reduced to ca. 5 mL and layered with hexane. After 2 d at 5° C, yellow crystals of **7a** were formed. Yield: 383 mg (63%). – IR ( $\text{CH}_2\text{Cl}_2$ ):  $\tilde{\nu}$  = 2089 (m)  $\nu(\text{C}\equiv\text{N})$ ; 1940 (s), 1902 (s),  $\nu(\text{CO})$ ; 1655 (m, br)  $\nu(\text{C}\equiv\text{N})$ . –  $^1\text{H}$  NMR (238 K):  $\delta$  = 1.69 [s, 6 H, xylyl- $\text{CH}_3$ ], 1.97 [s, 3 H, xylyl- $\text{CH}_3$ ], 2.23 [s, 3 H, xylyl- $\text{CH}_3$ ], 3.41 [m, 1 H, PCH<sub>A</sub>], 4.21 [m, 1 H, PCH<sub>B</sub>], 6.58–7.46 [m, 41 H, phenyl]. –  $^{31}\text{P}\{^1\text{H}\}$  NMR:  $\delta$  = 73.7 [dd,  $\text{P}^1(\text{Fe})$ ,  $^{2+3}J(\text{P}^1\text{-P}^2)$  = 163,  $^{3+4}J(\text{P}^1\text{-P}^3)$  = 4,  $^{2+3}J(\text{Pt-P})$  = 69 Hz], 41.7 [dd,  $\text{P}^3(\text{Pt})$ ,  $^2J(\text{P}^2\text{-P}^3)$  = 35,  $^1J(\text{Pt-P})$  = 4024 Hz], 31.8 [dd,  $\text{P}^2(\text{Pt})$ ,  $^1J(\text{Pt-P})$  = 2586 Hz]. –  $^{195}\text{Pt}\{^1\text{H}\}$  NMR:  $\delta$  = –2586 [ddd,  $^{2+3}J(\text{Pt-P}^1)$  = 75,  $^1J(\text{Pt-P}^2)$  = 2527,  $^1J(\text{Pt-P}^3)$  = 4264 Hz]. –  $\text{C}_{63}\text{H}_{55}\text{FeN}_2\text{O}_2\text{P}_3\text{Pt}$  (1216.0): calcd. C 62.23, H 4.56, N 2.30; found C 62.28, H 4.08, N 2.23.

**Preparation of [(OC)<sub>2</sub>(*p*-anisylNC)Fe(μ-C≡N–*p*-anisyl)(μ-dppm)Pt(PPh<sub>3</sub>)] (7b):** *p*-Anisyl isocyanide (133 mg, 1 mmol) was added to a stirred solution of **1a** (552 mg, 0.5 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL). The orange–red solution was stirred for 8 h at ambient temperature, then reduced to ca. 5 mL and layered with hexane. Yield: 454 mg (81%). – IR ( $\text{CH}_2\text{Cl}_2$ ):  $\tilde{\nu}$  = 2092 (m)  $\nu(\text{C}\equiv\text{N})$ ; 1942 (s), 1902 (s),  $\nu(\text{CO})$ ; 1653 (m, br)  $\nu(\text{C}\equiv\text{N})$ . –  $^1\text{H}$  NMR (243 K):  $\delta$  = 3.77 [s, 3 H,  $\text{OCH}_3$ ], 3.80 [s, 3 H,  $\text{OCH}_3$ ], 3.48 [m, vbr, not resolved, 1 H, PCH<sub>A</sub>], 4.25 [m, vbr, not resolved, 1 H, PCH<sub>B</sub>], 6.29–7.69 [m, 43 H, phenyl]. –  $^{31}\text{P}\{^1\text{H}\}$  NMR:  $\delta$  = 71.5 [dd,  $\text{P}^1(\text{Fe})$ ,  $^{2+3}J(\text{P}^1\text{-P}^2)$  = 162,  $^{3+4}J(\text{P}^1\text{-P}^3)$  = 5,  $^{2+3}J(\text{Pt-P})$  = 65 Hz], 41.7 [dd,  $\text{P}^3(\text{Pt})$ ,  $^2J(\text{P}^2\text{-P}^3)$  = 35,  $^1J(\text{Pt-P})$  = 4059 Hz], 30.3 [dd,  $\text{P}^2(\text{Pt})$ ,  $^1J(\text{Pt-P})$  = 2427 Hz]. –  $\text{C}_{61}\text{H}_{51}\text{FeN}_2\text{O}_4\text{P}_3\text{Pt}$  (1219.94): calcd. C 60.06, H 4.21, N 2.30; found C 60.09, H 4.35, N 2.55.

**Preparation of [(OC)<sub>3</sub>Fe(μ-CN(H)xylyl)(μ-dppm)Pt(PPh<sub>3</sub>)] [BF<sub>4</sub>] (8a):** This complex was prepared by adding excess  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  to a solution of **6a** (119 mg, 0.1 mmol) in  $\text{CH}_2\text{Cl}_2$  (5 mL) at 253 K. After warming to ambient temperature, all volatiles were removed under reduced pressure. The orange–red residue was rinsed with Et<sub>2</sub>O (3 mL) and dried in vacuo. Yield: 133 mg (97%). – IR ( $\text{CH}_2\text{Cl}_2$ ):  $\tilde{\nu}$  = 2036 (m), 1981 (vs), 1969 (vs)  $\nu(\text{CO})$ ; 1527 (w)  $\nu(\text{CN})$ . –  $^1\text{H}$  NMR:  $\delta$  = 2.18 [s, 6 H,  $\text{CH}_3$ ], 4.41 [t, 2 H,  $\text{CH}_2$ ,

$^2J(\text{P-H}) = 10.0$ ,  $^3J(\text{Pt-H}) = 39.5$  Hz], 6.89–7.69 [m, 38 H, phenyl], 9.18, [s, br, 1 H, NH]. –  $^{13}\text{C}\{^1\text{H}\}$  NMR:  $\delta = 313.7$  [dd,  $\mu\text{-C}$ ,  $^2J(\text{P-C}) = 77$ ,  $^2J(\text{P-C}) = 11$  Hz], 209.7 [d, 3 FeCO,  $^2J(\text{P-C}) = 19$  Hz], 128.1–134.2 [m, phenyl], 49.4 [m, unresolved, PCP], 18.1 [s, xylyl-CH<sub>3</sub>]. –  $^{31}\text{P}\{^1\text{H}\}$  NMR:  $\delta = 60.6$  [dd,  $\text{P}^1(\text{Fe})$ ,  $^{2+3}J(\text{P}^1\text{-P}^2) = 89$ ,  $^{3+4}J(\text{P}^1\text{-P}^3) = 13$ ,  $^{2+3}J(\text{Pt-P}) = 79$  Hz], 37.4 [dd,  $\text{P}^3(\text{Pt})$ ,  $^2J(\text{P}^2\text{-P}^3) = 4$ ,  $^{3+4}J(\text{P}^1\text{-P}^3) = 12$ ,  $^1J(\text{Pt-P}) = 3739$  Hz], 19.6 [dd,  $\text{P}^2(\text{Pt})$ ,  $^1J(\text{Pt-P}) = 2600$  Hz]. –  $^{195}\text{Pt}\{^1\text{H}\}$  NMR:  $\delta = -2456$  [ddd,  $^{2+3}J(\text{Pt-P}^1) = 79$ ,  $^1J(\text{Pt-P}^2) = 2600$ ,  $^1J(\text{Pt-P}^3) = 3739$  Hz]. –  $\text{C}_{55}\text{H}_{47}\text{BF}_4\text{FeNO}_3\text{P}_3\text{Pt} \cdot 2 \text{CH}_2\text{Cl}_2$  (1200.64 + 169.86): calcd. C 49.95, H 4.08, N 0.79; found C 49.40, H 3.99, N 0.97.

**Preparation of [(OC)<sub>3</sub>Fe( $\mu$ -CN(H)-*p*-anisyl)( $\mu$ -dppm)Pt(PPh<sub>3</sub>)](BF<sub>4</sub>) (8b):** This complex was prepared by adding excess HBF<sub>4</sub> · Et<sub>2</sub>O to a solution of **6c** (111 mg, 0.1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) at 253 K. After warming to ambient temperature, all volatiles were removed under reduced pressure. The orange–red residue was rinsed with Et<sub>2</sub>O (3 mL) and dried in vacuo. Yield: 115 mg (96%). – IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\tilde{\nu} = 2036$  (m), 1977 (vs)  $\nu(\text{CO})$ ; 1532 (w)  $\nu(\text{CN})$ . –  $^1\text{H}$  NMR:  $\delta = 3.84$  [s, 3 H, OCH<sub>3</sub>], 4.44 [t, 2 H, CH<sub>2</sub>,  $^2J(\text{P-H}) = 10.8$ ,  $^3J(\text{Pt-H}) = 40.0$  Hz], 6.81–7.79 [m, 39 H, phenyl], 9.45, [m, br, 1 H, NH]. –  $^{13}\text{C}\{^1\text{H}\}$  NMR:  $\delta = 306.8$  [dd,  $\mu\text{-C}$ ,  $^2J(\text{P-C}) = 76$ ,  $^2J(\text{P-C}) = 10$  Hz], 209.8 [d, 3 FeCO,  $^2J(\text{P-C}) = 18$  Hz], 115.2–159.8 [m, phenyl], 55.7 [s, OCH<sub>3</sub>], 49.3 [m, unresolved, PCP], 55.7 [s, OCH<sub>3</sub>]. –  $^{31}\text{P}\{^1\text{H}\}$  NMR:  $\delta = 57.2$  [dd,  $\text{P}^1(\text{Fe})$ ,  $^{2+3}J(\text{P}^1\text{-P}^2) = 89$ ,  $^{3+4}J(\text{P}^1\text{-P}^3) = 14$ ,  $^{2+3}J(\text{Pt-P}) = 81$  Hz], 37.1 [dd,  $\text{P}^3(\text{Pt})$ ,  $^2J(\text{P}^2\text{-P}^3) = 4$ ,  $^{3+4}J(\text{P}^1\text{-P}^3) = 14$ ,  $^1J(\text{Pt-P}) = 3716$  Hz], 18.0 [dd,  $\text{P}^2(\text{Pt})$ ,  $^1J(\text{Pt-P}) = 2583$  Hz]. –  $\text{C}_{54}\text{H}_{45}\text{BF}_4\text{FeNO}_4\text{P}_3\text{Pt}$  (1202.61): calcd. C 53.93, H 3.72, N 1.17; found C 53.60, H 3.45, N 1.07.

**Preparation of [(OC)<sub>3</sub>Fe( $\mu$ -CN(H)-*p*-C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>)( $\mu$ -dppm)Pt(PPh<sub>3</sub>)](BF<sub>4</sub>) (8c):** This complex was prepared by adding excess HBF<sub>4</sub> · Et<sub>2</sub>O to a solution of **6d** (110 mg, 0.1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) at 253 K. After warming to ambient temperature, all volatiles were removed under reduced pressure. The orange–red residue was rinsed with Et<sub>2</sub>O (3 mL) and dried in vacuo. Yield: 102 mg (93%). – IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\tilde{\nu} = 2036$  (m), 1977 (vs)  $\nu(\text{CO})$ . –  $^1\text{H}$  NMR:  $\delta = 2.35$  [s, 2 H, NH<sub>2</sub>], 4.45 [t, 2 H, CH<sub>2</sub>,  $^2J(\text{P-H}) = 10.0$ ,  $^3J(\text{Pt-H}) = 39.0$  Hz], 6.90–7.95 [m, 39 H, phenyl], 9.45 [s, br, 1 H, NH]. –  $^{31}\text{P}\{^1\text{H}\}$  NMR:  $\delta = 57.8$  [dd,  $\text{P}^1(\text{Fe})$ ,  $^{2+3}J(\text{P}^1\text{-P}^2) = 87$ ,  $^{3+4}J(\text{P}^1\text{-P}^3) = 15$ ,  $^{2+3}J(\text{Pt-P}) = 81$  Hz], 37.9 [d,  $\text{P}^3(\text{Pt})$ ,  $^{3+4}J(\text{P}^1\text{-P}^3) = 15$ ,  $^1J(\text{Pt-P}) = 3689$  Hz], 17.9 [d,  $\text{P}^2(\text{Pt})$ ,  $^1J(\text{Pt-P}) = 2581$  Hz]. – MS: (FAB<sup>+</sup>/diglyme matrix): 1100 M<sup>+</sup> (55%). –  $\text{C}_{53}\text{H}_{44}\text{BF}_4\text{FeN}_2\text{O}_3\text{P}_3\text{Pt} \cdot \text{Et}_2\text{O}$  (1187.60 + 74.12): calcd. C 54.26, H 4.31, N 2.22; found C 54.14, H 4.33, N 2.09.

**Collection of the X-ray Data and Structure Determination:** For **1b**, **6a**, and **6b** data were collected with a Siemens Stoe AED2 four-circle diffractometer using graphite-monochromated Mo- $K_\alpha$  radiation ( $\lambda = 0.71073$  Å). The final unit cell parameters were obtained by least squares on the setting angles for 20 reflections with  $2\theta = 20$ – $23^\circ$ . Data were corrected semiempirically for absorption correction using  $\Psi$  scans. SHELXS-97 and SHELXL-97 computer programs were used.<sup>[29]</sup> Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-114806–114808. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

**Crystal Structure Determination of 1b:** Collection of crystallographic data: intensity data were collected using the  $\Omega/2\theta$  scan mode at 293 K.  $\text{C}_{48}\text{H}_{46}\text{FeNO}_6\text{P}_3\text{PtSi}$  (1104.80): colorless crystals with approximate dimensions  $0.3 \times 0.2 \times 0.2$  mm, monoclinic,

space group  $P2_1/n$ ;  $a = 10.069(9)$ ,  $b = 18.475(10)$ ,  $c = 24.71(2)$  Å,  $\beta = 101.12(6)^\circ$ ,  $V = 4.510(6)$  Å<sup>3</sup>,  $Z = 4$ ,  $\rho_{\text{calcd.}} = 1.627$  g cm<sup>−3</sup>,  $F(000) = 2208$ ; 9351 independent reflections in the scan range  $1.68^\circ < 2\theta < 53.0^\circ$ , of which 9351 with  $I > 2\sigma(I)$  were used in the structure solution and refinement for 734 parameters;  $R1 = \Sigma|F_o - F_c|/\Sigma|F_o| = 0.0247$  [ $I > 2\sigma(I)$ ],  $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2} = 0.0603$  (all data), GoF = 1.034; anisotropic refinement for non-hydrogen atoms; hydrogen atoms in idealized geometries, except for H(1) and H(2), which were refined isotropically. Highest residual electron density  $1.105$  eÅ<sup>−3</sup>.

**Crystal Structure Determination of 6a:** Collection of crystallographic data: intensity data were collected using the  $\Omega/2\theta$  scan mode at 293 K.  $\text{C}_{56.5}\text{H}_{49}\text{Cl}_3\text{FeNO}_3\text{P}_3\text{Pt}$  (1240.17): orange crystals with approximate dimensions  $0.2 \times 0.3 \times 0.4$  mm, triclinic, space group  $P-1$ ;  $a = 12.08(2)$ ,  $b = 13.54(3)$ ,  $c = 18.60(3)$  Å,  $\alpha = 101.86(14)^\circ$ ,  $\beta = 100.72(13)^\circ$ ,  $\gamma = 111.81(12)^\circ$ ,  $V = 2646(8)$  Å<sup>3</sup>,  $Z = 2$ ,  $\rho_{\text{calcd.}} = 1.557$  g cm<sup>−3</sup>,  $F(000) = 1238$ ; 9172 independent reflections in the scan range  $1.90^\circ < 2\theta < 50.0^\circ$ , of which 8179 with  $I > 2\sigma(I)$  were used in the structure solution and refinement for 604 parameters;  $R1 = \Sigma|F_o - F_c|/\Sigma|F_o| = 0.0673$  [ $I > 2\sigma(I)$ ],  $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2} = 0.1871$  (all data), GoF = 1.075; anisotropic refinement for non-hydrogen atoms; hydrogen atoms in idealized geometries. Highest residual electron density  $2.653$  eÅ<sup>−3</sup>.

**Crystal Structure Determination of 6b:** Collection of crystallographic data: intensity data were collected using the  $\Omega/2\theta$  scan mode at 293 K.  $\text{C}_{54}\text{H}_{44}\text{FeNO}_3\text{P}_3\text{Pt}$  (1114.75): orange crystals with approximate dimensions  $0.4 \times 0.4 \times 0.3$  mm, monoclinic, space group  $P2_1/n$ ;  $a = 18.727(4)$ ,  $b = 12.668(3)$ ,  $c = 20.706(4)$  Å,  $\beta = 109.19(3)^\circ$ ,  $V = 4639(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $\rho_{\text{calcd.}} = 1.596$  g cm<sup>−3</sup>,  $F(000) = 2224$ ; 6968 independent reflections in the scan range  $1.79^\circ < 2\theta < 48.0^\circ$ , of which 6866 with  $I > 2\sigma(I)$  were used in the structure solution and refinement for 578 parameters;  $R1 = \Sigma|F_o - F_c|/\Sigma|F_o| = 0.0488$  [ $I > 2\sigma(I)$ ],  $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2} = 0.1466$  (all data), GoF = 1.200; anisotropic refinement for non-hydrogen atoms; hydrogen atoms in idealized geometries. Highest residual electron density  $2.621$  eÅ<sup>−3</sup>.

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- [1] [1a] C. Elschenbroich, A. Salzer, *Organometallchemie*, Teubner, Stuttgart, **1988**. – [1b] *Transition Metal Hydrides* (Ed.: A. Dedieu), VCH Publishers, Weinheim, New York, **1991**. – [1c] *Modern Acetylene Chemistry* (Eds.: P. J. Stang, F. Diederich), Wiley-VCH, Weinheim (Germany), **1995**.
- [2] [2a] D. L. Thorn, R. Hoffmann, *J. Am. Chem. Soc.* **1978**, *100*, 2079–2090. – [2b] N. M. Doherty, J. E. Bercaw, *J. Am. Chem. Soc.* **1985**, *107*, 2670–2682. – [2c] N. Koga, S.-Q. Jin, K. Morokuma, *J. Am. Chem. Soc.* **1988**, *110*, 3417–3425. – [2d] P. E. M. Siegbahn, *J. Am. Chem. Soc.* **1993**, *115*, 5803–5812. – [2e] W. R. Rocha, W. B. De Almeida, *Organometallics* **1998**, *17*, 1961–1967.
- [3] [3a] D. F. Christian, H. C. Clark, R. F. Stepniak, *J. Organomet. Chem.* **1976**, *112*, 209–225. – [3b] H. C. Clark, C. R. Jablonski, C. S. Wong, *Inorg. Chem.* **1975**, *14*, 1332–1335. – [3c] T. G. Attig, H. C. Clark, C. S. Wong, *Can. J. Chem.* **1977**, *55*, 189–198. – [3d] H. C. Clark, G. Ferguson, A. B. Goel, E. G. Janzen, H. Ruegger, P. Y. Siew, C. S. Wong, *J. Am. Chem. Soc.* **1986**, *108*, 6961–6972.



- [4] For further examples of olefin and alkyne insertions into Pt–H bonds see: [4a] J. Chatt, B. L. Shaw, *J. Chem. Soc.* **1962**, 21, 5075–5084. – [4b] R. Puddephatt, M. A. Thomsson, *Inorg. Chem.* **1982**, 21, 725–730. – [4b] C. Wieser, D. Matt, J. Fischer, A. Harriman, *J. Chem. Soc., Dalton Trans.* **1997**, 2391–2402. – [4c] L. M. Venanzi, in: *20 Int. Conf. Coord. Chem.*, 1979 (Ed.: D. Banjara), Pergamon, Oxford **1980**, pp. 99–105. – [4d] W. R. Meyer, L. M. Venanzi, *Angew. Chem. Int. Ed. Engl.* **1984**, 23, 529–531. – [4e] R. Ros, R. A. Michelin, R. Bataillard, R. Roulet, *J. Organomet. Chem.* **1979**, 165, 107–116. – [4f] C. M. Lukehart, W. R. True, *Organometallics* **1988**, 7, 2387–2393. – [4g] A. C. Dema, X. Li, C. M. Lukehart, M. D. Owen, *Organometallics* **1991**, 10, 1197–1200. – [4h] M. Gomez, G. Muller, D. Sainz, J. Sales, X. Solans, *Organometallics* **1991**, 10, 4036–4045. – [4i] L.-B. Han, M. Tanaka, *J. Am. Chem. Soc.* **1996**, 118, 1571–1572. – [4j] L.-B. Han, N. Choi, M. Tanaka, *Organometallics* **1996**, 118, 3259–3261. – [4k] A. Furiani, M. V. Russo, A. Chiesi Villa, A. G. Manfredotti, *J. Chem. Soc., Dalton Trans.* **1977**, 2154–2160. –
- For further examples of alkyne insertions into M–H bonds of heterobimetallic hydride complexes see: [4l] B. T. Sterenberg, R. McDonald, M. Cowie, *Organometallics* **1997**, 16, 2297–2312. – [4m] T. Sterenberg, R. W. Hiltz, G. Moro, R. McDonald, M. Cowie, *J. Am. Chem. Soc.* **1995**, 117, 245–258. – [4n] T. Yasuda, A. Fukuoka, M. Hirano, S. Komiya, *Chem. Lett.* **1998**, 29–30.
- [5] P. Braunstein, M. Knorr, A. Tiripicchio, M. Tiripicchio-Camellini, *Angew. Chem.* **1989**, 101, 1414–1416; *Angew. Chem. Int. Ed. Engl.* **1989**, 28, 1361–1363.
- [6] [6a] P. Braunstein, M. Knorr, U. Schubert, M. Lanfranchi, A. Tiripicchio, *J. Chem. Soc., Dalton Trans.* **1991**, 1507–1514. – [6b] J. Blin, P. Braunstein, J. Fischer, G. Kickelbick, M. Knorr, X. Morise, T. Wirth *J. Chem. Soc., Dalton Trans.* **1999**, 2159–2169.
- [7] P. Braunstein, E. Colomer, M. Knorr, A. Tiripicchio, M. Tiripicchio-Camellini, *J. Chem. Soc., Dalton Trans.* **1992**, 5, 903–909.
- [8] P. Braunstein, T. Faure, M. Knorr, T. Stährfeldt, A. De Cian, J. Fischer, *Gazz. Chim. Ital.* **1995**, 125, 35–50.
- [9] P. Braunstein, M. Knorr, C. Stern, *Coord. Chem. Rev.* **1998**, 178–180, 903–965.
- [10] M. Knorr, C. Strohmann, P. Braunstein, *Organometallics* **1996**, 15, 5653–5663.
- [11] [11a] B. E. Mann, B. L. Shaw, N. I. Tucker, *J. Chem. Soc. A* **1971**, 2103–2108. – [11b] P. J. Stang, Z. Zhong, M. Kowalski, *Organometallics* **1990**, 9, 833–838. – [11c] C. J. Cardin, D. J. Cardin, M. F. Lappert, *J. Chem. Soc., Dalton Trans.* **1977**, 767–778.
- [12] [12a] M. Knorr, P. Braunstein, A. De Cian, J. Fischer, *Organometallics* **1995**, 14, 1302–1309. – [12b] M. Knorr, P. Braunstein, A. Tiripicchio, F. Ugozzoli, *Organometallics* **1995**, 14, 4910–4919.
- [13] [13a] P. Braunstein, M. Knorr, E. Villarroya, A. De Cian, J. Fischer, *Organometallics* **1991**, 10, 3714–3722. – [13b] M. Knorr, P. Braunstein, A. Tiripicchio, F. Ugozzoli, *J. Organomet. Chem.* **1996**, 526, 105–116.
- [14] [14a] A. van Asselt, B. J. Burger, V. C. Gibson, J. E. Bercaw, *J. Am. Chem. Soc.* **1986**, 108, 5357–5349. – [14b] M. Olivan, E. Clot, O. Eisenstein, K. G. Caulton, *Organometallics* **1998**, 17, 3091–3100.
- [15] [15a] P. E. Garrou, R. F. Heck, *J. Am. Chem. Soc.* **1976**, 98, 4115–4127. – [15b] G. K. Anderson, R. J. Cross, *Acc. Chem. Res.* **1984**, 17, 67–74.
- [16] [16a] M. Ciriano, M. Green, D. Gregson, J. A. K. Howard, J. L. Spencer, F. G. A. Stone, P. Woodward, *J. Chem. Soc., Dalton Trans.* **1979**, 1294–1300. – [16b] N. W. Alcock, J. M. Brown, T. D. MacLean, *J. Chem. Soc., Chem. Commun.* **1984**, 1689–1691. – [16c] G. Facchin, P. Uguagliati, R. A. Michelin, *Organometallics* **1984**, 3, 1818–1822.
- [17] [17a] A part of this work has already been communicated: M. Knorr, T. Faure, P. Braunstein, *J. Organomet. Chem.* **1993**, 447, C4. – [17b] M. Knorr, C. Strohmann, *Organometallics* **1999**, 18, 248–257. – [17c] M. Knorr, C. Strohmann, *Eur. J. Inorg. Chem.* **1998**, 495–499. – [17d] M. Knorr, C. Strohmann, Poster abstract 98, *4th Anglo/German Inorganic Chemistry Meeting*, University of Marburg, **1997**. – [17e] M. Knorr, *Abstract B 32 Chemiedozententagung*, Universität GH Essen, **1998**.
- [18] [18a] E. Singleton, H. E. Oosthuizen, *Adv. Organomet. Chem.* **1983**, 22, 209–310. – [18b] D. Lentz, *Angew. Chem.* **1994**, 106, 1377–1393; *Angew. Chem. Int. Ed. Engl.* **1994**, 33, 1315–1331. – [18c] K. S. Ratliff, P. E. Fanwick, C. P. Kubiak, *Polyhedron* **1990**, 9, 2651–2653. – [18d] J. M. Basset, G. K. Barker, M. Green, J. A. K. Howard, F. G. A. Stone, W. C. Wolsey, *J. Chem. Soc., Dalton Trans.* **1981**, 219–227. – [18e] W. P. Fehlhammer, A. Mayr, W. Kehr, *J. Organomet. Chem.* **1980**, 197, 327–334. – [18f] W. P. Fehlhammer, A. Schröder, W. Sperber, J. Fuchs, *Chem. Ber.* **1992**, 125, 1087–1092. – [18g] M. O. Albers, A. A. Chalmers, G. J. Kruger, D. C. Liles, H. E. Oosthuizen, E. Singleton, N. J. Coville, *J. Organomet. Chem.* **1986**, 306, 385–394. – [18h] S. Bordonari, L. Busetto, M. C. Cassani, V. Zanotti, V. G. Albano, M. Monari, F. Prestopino, P. Sabatino, *Gazz. Chim. Ital.* **1995**, 125, 57–62. – [18i] R. D. Adams, F. A. Cotton, *Inorg. Chem.* **1974**, 13, 249–253. – [18j] F. A. Cotton, B. A. Frenz, *Inorg. Chem.* **1974**, 13, 253–256. – [18k] M. Ennis, R. Kumar, A. R. Manning, J. A. S. Howell, P. Mathur, A. J. Rowan, F. S. Stephens, *J. Chem. Soc., Dalton Trans.* **1981**, 1251–1259. – [18l] M. Sugimoto, Y. Kato, N. Takeda, H. Oike, Y. Ito, *Organometallics* **1998**, 17, 495–497. – [18m] Note that  $\mu$ -CNR ligands may also adopt a linear CN–R arrangement: Y. Yamamoto, H. Yamazaki, *Inorg. Chem.* **1986**, 25, 3327–3329.
- [19] J. A. Howell, J. Y. Saillard, A. L. Beuze, G. Jaouen, *J. Chem. Soc., Dalton Trans.* **1982**, 2533–2537.
- [20] N. M. Kostic, R. F. Fenske, *Organometallics* **1982**, 1, 974–982.
- [21] [21a] M. I. Bruce, *Chem. Rev.* **1991**, 91, 197–257. – [21b] A. B. Antonova, A. A. Johansson, *Russ. Chem. Rev.* **1989**, 58, 693–710. – [21c] A. B. Antonova, A. A. Johansson, N. A. Deykhina, E. D. Korniyets, N. I. Pavlenko, G. V. Burmakina, A. I. Rubaylo, A. G. Ginzburg, P. V. Petrovskii, *J. Organomet. Chem.* **1996**, 524, 81–85. – [21d] H. Werner, *Angew. Chem.* **1990**, 102, 1109–1121; *Angew. Chem. Int. Ed. Engl.* **1990**, 29, 1077.
- [22] P. S. Braterman, *Metal Carbonyl Spectra*, Academic Press, London, New York, **1975**.
- [23] [23a] M. J. Church, M. J. Mays, *J. Chem. Soc. A* **1968**, 3074–3078. – [23b] K. Thomas, J. T. Dumler, B. W. Renoe, D. M. Roundhill, *Inorg. Chem.* **1972**, 11, 1795–1799.
- [24] J. C. Bailar, H. Itatani, *Inorg. Chem.* **1965**, 4, 1618–1620.
- [25] U. Nagel, *Chem. Ber.* **1982**, 115, 1998–1999.
- [26] H. Nöth, E. Meinel, *Z. Anorg. Allg. Chem.* **1967**, 349, 225–240.
- [27] K. Sommer, *Z. Anorg. Chem.* **1970**, 376, 37–43.
- [28] I. Ugi, R. Meyr, *Chem. Ber.* **1960**, 93, 239–246.
- [29] G. M. Sheldrick, *SHELXL-97*, *SHELXS-97*, Universität Göttingen, Germany, **1997**.

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[199070]