Synthesis and Reaction Chemistry of Heterodi- and Heterotrimetallic Transition-Metal Complexes Based on 1-(Diphenylphosphanyl)-1'terpyridylferrocene

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The reaction of $[Fe(\eta^5-C_5H_4PPh_2)(\eta^5-C_5H_4terpy)]$ (5; terpy = 2,2':6',2''-terpyridin-4'-y]) with diverse transition-metal compounds including $[PtCl_2(Et_2S)_2]$, $[Pd(cod)X_2]$, [AuCl(tht)], [CuBr], $[Mo(CO)_4(nbd)]$, and $[{RhCl(cod)}_2]$ (X = Cl, Br; tht = tetrahydrothiophene; nbd = norbornadiene; cod = cyclooctadiene) to afford heterobi- and trimetallic complexes and a coordination polymer is reported. The following compounds were prepared: $[Fe(\eta^5-C_5H_4PPh_2\{PtCl_2(SEt_2)\})(\eta^5-C_5H_4terpy)]$ (7), $trans-[PtCl_2\{(Ph_2P-\eta^5-C_5H_4)(\eta^5-C_5H_4terpy)-Fe\}_2]$ (9), $[Fe(\eta^5-C_5H_4PPh_2PdCl_2)(\eta^5-C_5H_4terpy)]$ (12), $[Fe\{\eta^5-C_5H_4PPh_2(Cl_3Pd^-)](\eta^5-C_5H_4terpy)Fe\}_2]$ (16a, X = Cl; 16b, X = Br), $[Mo(CO)_4\{(\eta^5-C_5H_4PPh_2)(\eta^5-C_5H_4terpy)]_n$ (19), $[Fe\{\eta^5-C_5H_4Ph_2P(CuBr)\}(\eta^5-C_5H_4terpy)]_n$ (19), $[Fe\{\eta^5-C_5H_4Ph_2P(CuBr)](\eta^5-C_5H_4terpy)]_n$ (19), $[Fe\{\eta^5-C_5H_4Ph_2P(\Delta U)](\eta^5-C_5H_4terpy)]_n$ (19), $[Fe\{\eta^5-C_$

Introduction

In recent years, ferrocene-based organometallics have received remarkable attention because such molecules are in general very robust and show a reversible redox character.^[1] They are of interest in many fields of chemistry including organic synthesis, molecular recognition, material sciences, and homogeneous catalysis.^[2] Whereas symmetrically substituted ferrocenes with nitrogen,^[3] phosphorus,^[4] oxygen,^[5] or sulfur^[6] donor groups at the cyclopentadienyl rings are well studied, less is known about sandwich compounds that bear two different coordination functionalities.^[7] The latter type of molecules, with their asymmetric 1,1'-substitution pattern, are of great interest in, for example, homogeneous catalysis due to their hemilabile coordination sites.^[8] In this respect, the work of Gibson et al.,^[8a,9] Gimeno et al.,^[10] Keim et al.,^[11] Long et al.,^[7a,8a,9] and others^[12] must be mentioned, who recently reported about the systematic synthesis, reaction behavior, and characterization of P/S, P/O,

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 $\{Rh(cod)Cl\}(\eta^{5}-C_{5}H_{4}terpy)\}$ (23), $[Ru(\{\eta^{5}-C_{5}H_{4}Ph_{2}P(AuCl)\} (\eta^5 - C_5 H_4 \text{terpy}) Fe)_2 Cl_2$ (25),and [Fe{n⁵-C₅H₄PPh₂- $(PdCl_2)$ { η^5 -C₅H₄-CH=CHC(O)(py)}] (26). The molecular structures of 5, 9, 12, 14, 16b, 22, and 26 in the solid state are reported. They show typical features of related phosphanylferrocenes and terpyridylferrocenes. Characteristic of 12 is a C-H activation as a result of the close distance of palladium to the terpyridyl moiety. Complexes 12, 26, and [PdCl₂(dppf)] [dppf = 1,1'-bis(diphenylphosphanyl)ferrocene], for comparison, were used in preliminary studies as catalysts in the carbon-carbon coupling of iodobenzene with tert-butyl acrylate to give (E)-tert-butyl cinnamate. The conversion amounts to 80% with a turnover number of 160 and turnover frequency of 48 h⁻¹.

and N/O hemilabile ligand systems. First reports about the use of such asymmetric 1,1'-disubstituted ferrocenes in homogeneous catalysis were reported as well.^[7–9] One of the reports implied a chiral thioether-phosphanylferrocene, which was used in Pd-catalyzed allylic substitution of 1,3diphenylpropenyl acetate with malonate and nitrogen nucleophiles.^[13] The use of ferrocenes that contain unsymmetrical P/S or P/O ligands at the cyclopentadienyl rings as catalytic active species in combination with palladium(0) and palladium(II) reagents, respectively, were also tested by Gibson and Long in the Suzuki-Miyaura carboncarbon cross-coupling reaction of 4-bromotoluene with phenyl boronic acid to produce 4-methylbiphenyl.^[8a] Within this reaction the yield was doubled, when compared with the symmetrical 1,1'-bis(diphenylphosphanyl)ferrocene.

These studies have prompted us to prepare 1-(diphenylphosphanyl)-1'-terpyridylferrocene and to use this compound for the synthesis of transition-metal complexes of higher nuclearity. We chose this molecule as starting compound because the diphenylphosphanyl group should preferentially bind to soft and the terpyridyl unit to hard transition-metal-complex fragments.^[14] The application of the appropriate Fe–Pd-containing molecules in the Heck–Mizoroki reaction of iodobenzene with *tert*-butyl acrylate to give



(E)-tert-butyl cinnamate is reported as well. The molecular structures of seven compounds in the solid state are discussed.

Results and Discussion

To synthesize asymmetric 1,1'-substituted ferrocenebased heterodi- and heterotrimetallic FeM (M = Mo, Pd, Pt, Rh, Cu, Au), Fe_2M (M = Mo, Pd, Pt), Au₂Fe₂Ru, and PdFeNi complexes, we chose $[Fe(\eta^5-C_5H_4PPh_2)(\eta^5 C_5H_4$ terpy)] (5; terpy = 2,2':6',2''-terpyridin-4'-yl) as the key starting molecule, which is accessible by the reaction sequence shown in Scheme 1 including an aldol condensation [reaction (i)] and a Michael addition with subsequent ring closure [reaction (ii)]. Whereas molecules 1 and 5 are orange-colored, complex 3 is purple, most probably resulting from the α,β -unsaturated carbonyl pyridyl unit. Ferrocenes 3 and 5 could be isolated as solid materials that dissolve in common polar organic solvents. The unsymmetrical sandwich compound 5 is stable in the solid state and in solution, whereas it rapidly decomposes on exposure to light and hence should best be stored in the dark.



Scheme 1. Synthesis of **5** from **1**: (i) dichloromethane/ethanol mixture (1:5 v/v); NaOH, 25 °C, 2.5 h; (ii) ethanol, $[H_4N]OAc$, 100 °C, 3 h.

The molecular structure of **5** in the solid state was determined by single-crystal X-ray structure analysis, thus confirming the structural assignment made from spectroscopic characterization (see Exp. Section). Single crystals of this compound were obtained by diffusion of *n*-pentane into a saturated solution of **5** in dichloromethane at room temperature. The molecular structure of **5** and selected bond distances [Å] and angles [°] are presented in Figure 1. The crystal and structure refinement data are summarized in Table 3 (see Exp. Section).

Ferrocene 5 represents a unsymmetrical 1,1'-disubstituted sandwich molecule in which a diphenylphosphanyl and a terpyridyl ligand are bonded to individual cyclopentadienyl rings. They are rotated by $85.0(3)^\circ$ to each other (Figure 1). The C₅H₄ rings are inclined by $3.0(3)^\circ$ and are



Figure 1. ORTEP diagram of **5**. Thermal ellipsoids are shown at the 50% probability level. The hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [°]: Fe1–D1 1.647(3), Fe1–D2 1.648(3), P1–C1 1.814(5), P1–C11 1.836(6), P1–C17 1.829(5), C6–C23 1.479(6); P1–C1–C2 130.6(4), P1–C1–C5 123.2(4), C11–P1–C17 102.3(2), C1–P1–C17 100.7(2); D1: centroid of C1–C5, D2: centroid of C6–C10.

staggered by 9°. The geometry at P1 is distorted tetrahedral with angles in the range of $100.7(2)-102.3(2)^{\circ}$ (Figure 1). The 2,2':6',2''-terpyridyl group adopts, as expected, a trans-trans conformation about the interannular C25-C28 and C26-C33 bonds.^[15] In addition, the terpy group is nearly planar [root mean-square deviation (RMSD) from planarity = 0.068 Å]. The interplanar angle between the cyclopentadienyl ring C6-C10 and N1, C23-C27 is 11.1(3)°, thereby showing that both groups are not coplanar to each other (Figure 1). The bonds and angles about the ferrocene, diphenylphosphanyl, and terpyridyl building blocks are similar to those typically found for this type of fragments.^[16] As a guide to the coordination properties of **5**, we treated it with diverse transition-metal complexes including $[PtCl_2(Et_2S)_2]$, $[Pd(cod)X_2]$, $[Mo(CO)_4(nbd)]$, [CuBr], [AuCl(tht)], and [{RhCl(cod)}₂] (X = Cl, Br; nbd = norbornadiene; tht = tetrahydrothiophene; cod = cyclooctadi-1.5-ene).

The appropriate FePt compound [Fe(n⁵-C₅H₄PPh₂- ${PtCl_2(SEt_2)})(\eta^5-C_5H_4terpy)$ (7) was formed by treatment of 5 with equimolar amounts of $[PtCl_2(SEt_2)_2]$ (6) in dichloromethane as solvent at ambient temperature (Scheme 2). Exclusive coordination of the diphenylphosphanyl group to platinum is observed. Since unsymmetrical substituted 7 possesses with the Et₂S donor group a labile ligand,^[17] we treated it with a further equivalent of 5. After appropriate workup, the expected trimetallic Fe₂Pt complex 9 (Scheme 2) could be isolated as an orange solid in 89% yield (see Exp. Section). The latter molecule was also formed when 7 was treated with triphenylphosphane. The in situ formed unsymmetrical complex $[{Pt(Cl)_2(PPh_3)}]$ -{Fe(η^5 -C₅H₄PPh₂)(η^5 -C₅H₄terpy)}] rapidly exchanges its ligands to give 9 and the respective [Pt(PPh₃)₂Cl₂] species, a common feature of $[Pt(L)(L')Cl_2]$ complexes (L, L' = 2electron donors).



Scheme 2. Synthesis of 7 and 9 from 5 and 6: (i) 25 °C, 10 min, dichloromethane; (ii) 25 °C, 30 min, tetrahydrofuran.

The identities of **7** and **9** have been confirmed by elemental analysis, ¹H and ³¹P{¹H} NMR spectroscopy, and ESI-TOF mass spectrometry (**9**). The molecular structure of **9** in the solid state was additionally measured by single-crystal X-ray structure determination (Figure 2).

The ³¹P{¹H} NMR spectrum of **5** displays a resonance signal at $\delta = -18.3$ ppm due to the presence of the noncoordinating Ph₂P unit. The P-coordination of the diphenyl-phosphane moiety to a [PtCl₂(SEt₂)] fragment in **7** or a PtCl₂ unit in **9** is best reflected by a significant shift to lower field (**7**, $\delta = 14.9$ **9**, 10.0 ppm). The signals thereby show a characteristic coupling with ¹⁹⁶Pt ($I = \frac{1}{2}$, 25.3% abundance) giving doublets with typical ¹*J*_{31P,196Pt} coupling constants of 3690 (**7**) and 2630 Hz (**9**). These values are in agreement with the coupling data found in other square-planar platinum–diphosphanyl complexes with *trans* geometry.^[18]

The formation of **7** is also confirmed by ¹H NMR spectroscopy since two new resonances for the [PtCl₂(SEt₂)] coordination fragment can be observed at $\delta = 1.08$ (CH₃) and 2.50 ppm (CH₂) with ³J_{H,H} = 7.2 Hz. On replacement of SEt₂ by a second [Fe(η^{5} -C₅H₄PPh₂)(η^{5} -C₅H₄terpy)] unit,

these two resonances disappear and the progress of the reaction can therefore easily be controlled by ¹H NMR spectroscopy.

The formation of **9** is additionally evidenced from ESI-TOF mass spectrometric investigations, which indicate the presence of the molecular ion $[M + H]^+$ at a mass-to-charge ratio (*m*/*z*) of 1468.90 (see Exp. Section).

Single crystals of **9** were obtained from slow diffusion of *n*-pentane into a saturated solution of **9** in dichloromethane at 25 °C. The molecular structure of **9** is shown in Figure 2. The crystal and structural refinement data are summarized in Table 3 (see Exp. Section). Compound **9**, as the 2:1 adduct of **5** and PtCl₂, crystallized in the monoclinic centrosymmetric space group P_{21}/c with crystallographically imposed inversion symmetry at Pt1. The platinum atom is coordinated by two chlorido and two phosphorus atoms in a precisely planar geometry. For compound **9**, an identical rotation of the Ph₂P versus terpyridyl moieties, as discussed for **5**, has been observed. The cyclopentadienyl rings are inclined by 3.8(3)° and staggered by approximately 3–5°. Due to the Pt–P bond the angles around P1 are more open



Figure 2. ORTEP diagram (50% probability level) of the molecular structure of **9**. The hydrogen atoms are omitted for clarity. Symmetry transformations used to generate equivalent atoms labeled with A: -x, -y, -z + 1. Selected bond distances [Å] and angles [°]: Fe1–D1 1.650(2), Fe1–D2 1.653(2), P1–C1 1.827(3), P1–C13 1.803(4), P1–C7, C18–C23 1.473(5); Pt1–C11 2.301(1), Pt1–P1 2.322(1); C7–P1–C1 104.52(15), C13–P1–C1 102.14(16), C11–Pt1–P1 88.47(4) C1–P1–Pt1 112.15(11); D1: centroid of C13–C17, D2: centroid of C18–C22.

relative to 5 and range from $104.5(2)-116.7(1)^{\circ}$. This is in a good agreement with the observations made in similar systems.^[7a]

A further possibility to prepare heterodi- (FePd) and heterotrimetallic (Fe₂M; M = Mo, Pd) transition-metal complexes based on 5 is given by the reactions depicted in Scheme 3. In this respect, we treated 5 with the palladium source [PdCl₂(cod)] in an equimolar amount, whereby dark orange 12 was formed in good yield (see Exp. Section). In 12, the square-planar coordination geometry of the palladium(II) ion is set up by two trans-oriented chlorido ligands, the diphenylphosphanyl group, and one pyridyl ligand of the terpyridyl moiety. When molecule 12 was further treated with a third transition-metal salt such as [NiCl₂(dme)] (13; dme = dimethoxyethane) in tetrahydrofuran, a dark red precipitate was formed. After appropriate workup, and addition of dimethyl sulfoxide (dmso), zwitterionic heterotrimetallic 14 could be isolated in which a $[PdCl_3(Ph_2P)]^-$ fragment and a [Ni(Cl)(dmso)₂(terpy)]⁺ ion are connected by the Fe(η^5 -C₅H₄)₂ sandwich backbone (Scheme 3). A somewhat different reaction behavior was found when 5 was treated with $[ML_nL']$ [11a, M = Pd, L = Cl, L' = cod, n = 2; 11b, M = Pd, L = Br, L' = cod, n = 2; 15, M = Mo, L = CO, L' = nbd, n = 4] in a 2:1 molar ratio (Scheme 3). Treatment of 5 with 11a or 11b exclusively gave trans- $[PdL_{2}{(\eta^{5}-C_{5}H_{4}Ph_{2}P)(\eta^{5}-C_{5}H_{4}terpy)Fe}_{2}]$ (16a, L = Cl; 16b, L = Br), which could be isolated as an orange solid material in 84% yield (Scheme 3, Exp. Section). Complex $[Mo(CO)_4{(\eta^5-C_5H_4PPh_2)(\eta^5-C_5H_4terpy)Fe}_2]$ (17) was prepared by combining 5 with 15, whereby nbd was concomitantly eliminated from 15 (Scheme 3).

Complexes 16 and 17 are barely soluble in common organic solvents (dichloromethane, tetrahydrofuran). Compound 14 is, due to its zwitterionic nature, only moderately soluble in dmso. Due to the insufficient solubility of 16 and 17, no ${}^{13}C{}^{1}H$ NMR spectra could be obtained. As a result of the paramagnetic character of **14** (octahedral-coordinated Ni^{II}), no standard NMR spectroscopic measurements could be performed.

As expected, 16 and 17 show different spectral features from 12 because in 12 the terpyridyl moiety asymmetrically coordinates with one of its pyridyl units to the Pd^{II} ion. That is why for the terpyridyl ligand two sets of signals are found in the ¹H and ¹³C{¹H} NMR spectra (Exp. Section). It is noteworthy that the hydrogen atom at C24 (see X-ray structure determination, Figure 3) is found at δ = 10.46 ppm and is significantly shifted to lower field when compared with the chemical shift of the hydrogen atom bonded to C26 (δ = 8.61 ppm). An explanation for this behavior is the close proximity (2.55 Å) of the respective hydrogen atom to palladium, which could be confirmed by Xray structure analysis (vide infra). For all other species, the expected signal and coupling patterns are observed (Exp. Section). A representative ¹H NMR spectrum of 12 is depicted in Figure 3; for comparison the ¹H NMR spectrum of 5 is presented as well.

From ³¹P{¹H} NMR spectroscopic studies it is clear that the diphenylphosphanyl groups in **12**, **16**, and **17** are datively bonded to the transition metals palladium and molybdenum, respectively, since a distinct downfield shift is observed ($\delta = 14-26$ ppm) relative to **5** ($\delta = -18.3$ ppm; see Exp. Section).

Less information can be obtained from IR spectroscopic studies of **12**, **14**, **16a**, and **16b**, whereas the metal carbonyl building block in **17** shows the characteristic strong absorptions typical for a $[Mo(CO)_4]$ fragment ($\tilde{v}_{CO} = 2018, 1900, 1867, 1812 \text{ cm}^{-1}$), thereby indicating a *cis* coordination^[19] of the two bulky $[Fe(\eta^5-C_5H_4PPh_2)(\eta^5-C_5H_4terpy)]$ moieties.

Figures 4, 5, and 6 highlight the solid-state structures and selected bond lengths [Å] and angles [°] of **12** (Figure 4), **14** (Figure 5), and **16b** (Figure 6). X-ray-quality single crystals of these molecules could be grown by diffusion



Scheme 3. Synthesis of **12**, **14**, **16**, and **17** from **5**: (i) dichloromethane, 30 min, 25 °C; (ii) tetrahydrofuran, 1 min, 25 °C, recrystallization from dmso; (iii) dichloromethane, 10 min, 25 °C.



Figure 3. ¹H NMR spectra of 5 (top) and 12 (below) (in CDCl₃, 25 °C, 250 MHz).

of *n*-hexane into solutions of **12** or **16b** in chloroform, whereas crystals of **14** were obtained by diffusion of diethyl ether into a mixture of dmso/dichloromethane in a ratio of 70:30 (v/v) at ambient temperature. The crystal and structure refinement data of **12**, **14**, and **16b** are summarized in Table 3 (see Exp. Section).



Figure 4. ORTEP diagram of **12**. Thermal ellipsoids are shown at the 50% probability level. All hydrogen atoms, except H24, and the disordered tetrahydrofuran molecule as noncoordinating packing solvent have been omitted for clarity. Selected bond lengths [Å], angles [°], and torsion angles [°]: Fe1–D1 1.663(3), Fe1–D2 1.661(3), Pd1–P1 2.2413(16), Pd1–N2 2.146(6), Pd1–Cl1 2.3101(16), Pd1–Cl2 2.3128(16), P1–C1 1.803(6), C6–C25 1.468(9); C1–P1–Pd1 116.4(2), N2–Pd1–P1 175.44(17), C11–Pd1–Cl2 177.87(6), P1–Pd1–Cl1 94.97(6), Pd1–N2–C28 124.2(5); N1–C23–C28–N2 –140.8(6), N1–C27–C33–N3 –177.3(6); D1: centroid of C1–C5, D2: centroid of C6–C10.

Crystallographic data of **12** reveal an almost squareplanar geometry about the Pd^{II} center. The sum of the angles around Pd1 is essentially 360° with *trans*-oriented chlorido ligands. The Pd1–Cl1 and Pd1–Cl2 bond lengths of 2.3101(16) and 2.3128(16) Å, respectively, are comparable with bond separations observed for other palladium dichloride molecules that feature phosphane and/or pyridyl ligands.^[20] As expected, the Pd1–P1 distance [2.2413(16) Å] is shorter than in *trans*-bis(phosphanyl)palladium(II) complexes (i.e., 2.325 Å),^[20b] whereas the respective Pd1–N2 separation found in **12** [2.146(6) Å] is long compared to distances that involve Pd–N bonds that are *trans* oriented (i.e., 2.007 Å).^[21] This can be explained by the *trans* influence.^[22] The two noncoordinated pyridyl rings of the terpy unit are found to be in-plane-bonded with the cyclopentadienyl ring C6–C10 (RMSD 0.070 Å) (Figure 4). The pyridyl ring coordinated to Pd1 is twisted by about 36.9(9)° from this plane. The unusual chemical shift of the hydrogen atom bonded to C24 can be explained by the short Pd1–H24 distance, which is with 2.55 Å shorter than the sum of palladium and hydrogen van der Waals radii (2.8 Å).^[23]

The overall structural features of 14 are similar to those of related structurally characterized molecules containing (diphenylphosphanyl)ferrocene, terpyridylferrocene, palladium chloride, and nickel chloride.^[20,21,24] Complex 14 consists of a 1-(diphenylphosphanyl)-1'-terpyridylferrocene centrality with a distorted square-planar Pd1, Cl1-Cl3, P1 fragment and a distorted octahedrally coordinated Ni^{II} ion (Ni1, Cl4, O1, O2, N1-N3) (Figure 5). The Cl1-Pd1-Cl3 angle [170.78(8)°] is reduced from 180° as a result of the steric demand of the organometallic $[Fe(\eta^5-C_5H_4PPh_2)(\eta^5 C_5H_4$ terpy{NiCl(dmso)₂})] building block. As expected, the Pd1-Cl2 bond length of 2.399(3) Å is longer than the appropriate Pd1-Cl1 [2.296(2) Å] and Pd1-Cl3 separations [2.297(3) Å] that are *trans*-oriented to ligands with a *trans* influence weaker than phosphorus.^[22] The cylopentadienyl rings of the ferrocenyl moiety are rotated by around 3°, which verifies an almost eclipsed conformation. The Fe-D distances (D is the centroid of the respective cyclopentadienyls) are characteristic^[25] and indicate that the iron atoms are almost equidistant from the cyclopentadienyl rings and correspond to those bond lengths found for other ferrocenes.^[20b] The coordination sphere about Ni1 is set up by a terpy (N1–N3) and one dmso (O2) ligand in equatorial positions, and Cl4 as well as the second dmso solvent molecule localized in axial positions (Figure 5). The Ni1-O2 bond [2.052(5) Å] is shorter than the Ni1–O1 distance [2.105(6) Å], thus indicating the *trans* influence of pyridyl and chloride ligands, respectively (Figure 5). The best planes of the terpy group and the cyclopentadienyl C6-C10 ring are rotated by 11.7(4)° to each other. The bond lengths and bond angles about the phosphanyl and terpy substituents are close to those reported for analogous transitionmetal building blocks.[20,21,25]



Figure 5. ORTEP diagram of 14. Thermal ellipsoids are shown at the 50% probability level. The hydrogen atoms and the disordered dichloromethane molecule as noncoordinating packing solvent are omitted for clarity. Selected bond lengths [Å], angles [°], and torsion angles [°]: Fe1–D1 1.6541(7), Fe1–D2 1.6552(8), Pd1–P1 2.252(3), Pd1–Cl1 2.296(2), Pd1–Cl3 2.297(3), Pd1–Cl2 2.399(3), P1–C1 1.803(10), C6–C23 1.457(11); Ni1–N1 1.987(6), Ni1–N2 2.124(6), Ni1–N3 2.106(6), Ni1–O1 2.105(6), Ni1–O2 2.052(5), Ni1–Cl4 2.390(2); P1–Pd1–Cl1 89.68(10), C11–Pd1–Cl3 170.78(8), P1–Pd1–Cl2 176.08(8), N1–N11–O2 171.5(2), N3–Ni1–N2 156.8(2), O1–Ni1–Cl4 176.31(16), N3–Ni1–Cl4 90.31(19); N1–C26–C33–N3–0.2(11), N1–C25–C28–N2 4.1(10), C7–C6–C23–C24–8.1(13); D1: centroid of C1–C5, D2: centroid of C6–C10.



Figure 6. ORTEP diagram of **16b**. Thermal ellipsoids are shown at the 50% probability level (symmetry transformations used to generate equivalent atoms: -x, -y, -z + 1; center of inversion on Pd1). The hydrogen atoms are omitted for clarity. Selected bond lengths [Å], angles [°], and torsion angles [°]: Fe1–D1 1.646(3), Fe1–D2 1.643(3), Pd1–P1 2.3304(17), Pd1–Br1 2.3969(8), P1–C1 1.785(6), C6–C23 1.466(10); P1–Pd1–Br1 88.77(4), C1–P1–Pd1 115.7(2); C7–C6–C23–C24, N1–C25–C28–N3 175.5(5), N1–C26–C33–N2 –173.6(8); D1: centroid of C1–C5, D2: centroid of C6–C10.

The single-crystal X-ray structure analysis of **16b** shows nearly the same structural features as discussed for **5** and **9** (see Figures 1 and 2). Complex **16b** crystallized in the monoclinic centrosymmetric space group $P2_1/c$ with crystallographically imposed inversion symmetry at Pd1. The platinum atom is coordinated in a planar geometry by two bromides and two phosphorus atoms. The cyclopentadienyl rings are inclined by 3.7(5)° and staggered by 3–5°.

Treatment of a solution of **5** in tetrahydrofuran with the copper(I) salt [CuBr] (**18**) resulted in the formation of coordination polymer **19** in virtually quantitative yield (Scheme 4, Exp. Section). Elemental analysis of **19** is in good agreement with the proposed composition. The ³¹P{¹H} NMR spectrum of **19** is indicative of the coordination of the diphenylphosphanyl group to copper(I) because a typical chemical shift from $\delta = -18.3$ (**5**) to -14.9 ppm (**19**) is found.^[26] A broad signal is observed that is attributed to

the two isotopes of copper (63 Cu, 65 Cu).^[27] Coordination of the terpy group to copper(I) was proven by ¹H NMR spectroscopy. The signals for the terpy ligand are shifted to a lower field than that of the starting material **5** [C₅H₂N: δ = 8.46 ppm (**5**); 8.53 ppm (**19**)] (see Exp. Section). Due to this, we postulate that **19** is polymerically constructed. On addition of dmso, complex **19** was transformed to a species of composition [Fe(η^{5} -C₅H₄Ph₂P{CuBr(dmso)_n})(η^{5} -C₅H₄terpy)], which affirms the postulation of a coordination polymer.

Organometallic **5** as a multitopic molecule with the Lewis basic diphenylphosphanyl and terpyridyl units to allow mono-, bi-, and/or tridentate coordination of different organometallic coordination fragments (vide supra) was also treated with tetrahydrothiophene gold(I) chloride (**20**) in tetrahydrofuran as solvent at 25 °C (Scheme 4). Within this reaction the weakly bonded tht ligand is replaced by



Scheme 4. Reaction chemistry of 5 towards [CuBr], [AuCl(tht)], and [{RhCl(cod)}₂]: (i) tetrahydrofuran, 2 h, 25 °C; (ii) ethanol, 12 h, reflux.

the stronger donor/acceptor group PPh₂. After appropriate workup, pale yellow [Fe{ η^5 -C₅H₄Ph₂P(AuCl)}(η^5 -C₅H₄terpy)] (**22**) was obtained in high yield (Exp. Section). Heterobimetallic (FeRh) **23** could be prepared by treatment of **5** with [{RhCl(cod)}₂] (**21**) in a 1:1 molar ratio in tetrahydrofuran (Scheme 4).

Compounds 22 and 23 were characterized by elemental analysis and IR and NMR spectroscopy. NMR spectroscopic properties of both complexes correlate with their formulation as heterodimetallic FeM complexes (M = Au, Rh). The identity of 22 was further confirmed by single-crystal X-ray diffraction studies.

For compound 22, X-ray quality crystals could be obtained by slow diffusion of *n*-pentane into a solution of 22 in dichloromethane at ambient temperature. The molecular structure of 22 is presented in Figure 7 together with selected bond lengths [Å] and angles [°]. The crystal and structure refinement data are summarized in Table 4 (Exp. Section).

Molecule **22** crystallized in the triclinic space group $P\overline{1}$. The structure of **22** shows a linear geometry around Au1 set up by the Ph₂P and Cl ligands, and Fe1 as part of a sandwich structure. Geometrical parameters within the Ph₂PAuCl fragment and the ferrocenyl–terpy building block are similar to those reported previously in comparable molecules.^[16,28] As observed for **5**, also in **22** the terpyridyl moiety adopts a *trans–trans* conformation. In contrast to **5**, the terpyridyl moiety is not planar. Calculated interplanar angels between the C₅H₄N groups range from 7.7(2) (N1, C23–C27 vs. N3, C33–C37) to 20.6(2) ° (N1, C23–C27 vs. N2, C28–C32).

Coordination of the terpyridyl donor group in **22** to ruthenium using [RuCl₂(dmso)₄] as the ruthenium source gave pentametallic (Au₂Fe₂Ru) **25**. In this molecule, two units of **22** are bridged through the coordination of their terpyridyl moieties to the centered ruthenium(II) ion, which was proven by ¹H NMR spectroscopy [C₅H₂N: δ = 8.35 ppm (**22**), 9.67 ppm (**25**)].



Figure 7. ORTEP diagram of **22**. Thermal ellipsoids are shown at the 50% probability level. The hydrogen atoms are omitted for clarity. Selected bond lengths [Å], angles [°], and torsion angles [°]: Fe1–D1 1.631(1), Fe1–D2 1.644(1), Au1–Cl1 2.2616(9), Au1–P1 2.2154(7), P1–C1 1.773(3), C6–C23 1.470; P1–Au1–Cl1 178.29(4), Au1–P1–C1 113.78(9); N1–C26–C33–N3 172.2(2), N1–C25–C28–N2 161.2(3), C7–C6–C23–C24 170.1(3); D1: centroid of C1–C5, D2: centroid of C6–C10.

For catalytic purposes, we treated **3** with equimolar amounts of **11a** [Reaction (1)]. The PdFe molecule **26** formed in this way was obtained as a deep purple solid.



Characterization of **26** is based on elemental analysis, spectroscopy (NMR, IR) and mass spectrometry (ESI-TOF) (see Exp. Section) as well as single X-ray structure analysis (Figure 8, Table 1).



Figure 8. ORTEP diagram (50% probability level) of the molecular structure of **26** forming a solvent-bridged centrosymmetric dimer in the solid state, due to the formation of hydrogen bonds. All carbon-bonded hydrogen atoms have been omitted for clarity. Symmetry operations used to generate equivalent atoms are labeled with A: -x + 2, -y + 2, -z. Selected bond lengths [Å] and angles [°]: Fe1–D1 1.634(4), Fe1–D2 1.648(4), Pd1–P1 2.2443(5), Pd1–N1 2.1337(13), Pd1–Cl1 2.2935(4), Pd1–Cl2 2.3073(4), C6–C23 1.453(2), C23–C24 1.341(2), P1–Pd1–N1 175.03(4), C11–Pd1–Cl2 175.379(15), C11–Pd1–P1 88.14(4), Cl2–Pd1–N1 87.85(4); D1: centroid of C1–C5, D2: centroid of C6–C10.

Table 1. Bond lengths [Å] and angles $[\circ]$ of the intermolecular hydrogen bonds of **26** (D: donor, A: acceptor).

D–H···A	D–H [Å]	H…A [Å]	D…A [Å]	D–H…A [°]
02–H10····O1	0.82(5)	2.09(5)	2.907(3)	176(4)
02A–H2OA····O1	0.75(5)	2.21(5)	2.958(3)	175(6)

Crystallization of 26 was carried out in untreated solvents; it resulted in the presence of water in the solid-state structure. Compound 26 crystallized as a centrosymmetric dimer in which two water molecules bridge two molecules of 26 by the formation of intermolecular hydrogen bonds by molecular recognition.

The PdCl₂NP coordination setup is almost planar, as the sum of all angles around Pd1 is $359.9(5)^\circ$, with *trans*-oriented chlorido ligands. The Pd1–Cl1 and Pd1–Cl2 bond lengths of 2.2935(4) and 2.3073(4) Å are comparable with distances of related complexes.^[20b]

In a preliminary study, heterobimetallic transition-metal complexes **12** and **26** were screened for their catalytic activities in the Heck–Mizoroki reaction.^[29] The results obtained (rate of conversion, kinetic studies) are summarized in Table 2 and Figure 9. To test the productivity of these two organometallic species, we treated iodobenzene (**27**) with *tert*-butyl acrylate (**28**) to give (*E*)-*tert*-butyl cinnamate (**29**) in toluene and acetonitrile mixtures of ratio 1:1 (v/v) at 80 °C in presence of EtN*i*Pr₂ as a base and as reducing agent with a catalyst loading of 0.5 mol-% [see reaction (2), Table 2, Figure 9]. In addition to these studies, reactions

Table 2. Conditions of the Heck–Mizoroki carbon–carbon crosscoupling reaction of **27** with **28** by complexes **12**, **26**, and **30** for comparison (conc. 0.5 mol-%, 80 °C, 25 h).

Compound	Yield of 29 [%] ^[a]	TON ^[b]	TOF [h ⁻¹] ^[b]
12	79	158	48
26	81	162	42
30	50	100	23

[a] Yields have been measured by ¹H NMR spectroscopy with acetylferrocene as internal standard. [b] TON = turnover number. Turnover frequencies (TOFs) are determined after one hour. with the conventional $[PdCl_2(dppf)]$ system [dppf = 1,1'-bis(diphenylphosphanyl) ferrocene] (30) were carried out so that direct comparison might be achieved.



Figure 9. Kinetic investigations of **12**, **26**, and **30** (for comparison) in the Heck–Mizoroki carbon–carbon cross-coupling of **27** with **28** (0.5 mol-% catalyst, 80 °C).



As summarized in Table 2 and Figure 9, the maximum possible conversion amounts to 80%. As a consequence of these data, it can be concluded that a higher productivity is obtained with catalysts possessing hemilabile ligands as given in complexes **12** and **26** when compared to an analogous symmetrical diphosphane such as dppf.

Conclusion

A new ligand system based on a ferrocenyl backbone that features a terpyridyl and a diphenylphosphanyl donor group is described using consecutive synthesis methodologies. A series of novel heterobi- and heterotrimetallic complexes including $[Fe(\eta^5-C_5H_4Ph_2\{PtCl_2(SEt_2)\})(\eta^5-$ C₅H₄terpy)], trans-[PtCl₂{ $(\eta^5$ -C₅H₄Ph₂P)(η^5 -C₅H₄terpy)-Fe}₂], [Fe{ η^{5} -C₅H₄-PPh₂(Cl₂Pd)}(η^{5} -C₅H₄terpy)], [Fe{ η^{5} - $C_5H_4PPh_2(Cl_3Pd^{-})$ {(η^5 - C_5H_4 terpy{(dmso)₂-ClNi⁺})], trans- $[PdX_2{(\eta^5-C_5H_4Ph_2P)(\eta^5-C_5H_4terpy)Fe}_2]$ (X = Cl, Br), $[Mo(CO)_4{(\eta^5-C_5H_4PPh_2)(\eta^5-C_5H_4terpy)Fe}_2],$ $[Fe{\eta^5} [Fe{\eta^5-C_5H_4Ph_2P C_5H_4Ph_2P(CuBr)\}(\eta^5-C_5H_4terpy)]_n$ (AuCl) $(\eta^5-C_5H_4terpy)$, [Fe $(\eta^5-C_5H_4Ph_2P\{Rh(cod)Cl\})$ - $(\eta^{5}-C_{5}H_{4}terpy)], [Ru(\{\eta^{5}-C_{5}H_{4}Ph_{2}P(AuCl)\}(\eta^{5}-C_{5}H_{4}terpy) [Fe{\eta^5-C_5H_4PPh_2(PdCl_2)}{\eta^5-C_5H_4-}$ $Fe_{2}Cl_{2}$ and CH=CHC(O)(py)}] have been synthesized by treatment of $[PtCl_2(Et_2S)_2]$, $[Pd(cod)X_2]$, [AuCl(tht)], [CuBr], $[Mo(CO)_4$ -(nbd)], and [{Rh(cod)Cl}₂] with [Fe(η^5 -C₅H₄PPh₂)(η^5 - C_5H_4 terpy)] and [Fe(η^5 - $C_5H_4PPh_2$){ η^5 - C_5H_4 -CH=CHC-(O)(py)}], respectively. Seven compounds have been structurally characterized by single-crystal X-ray diffraction analysis. The appropriate molecules show typical features known for related phosphanylferrocenes and terpyridylferrocenes.^[16] The phosphanyl and terpyridyl groups are oppositely oriented except for complex 12, due to the chelating P/N coordination. A carbon-hydrogen bond activation could be observed for 12 as a result of the close distance of the palladium atom to the terpyridyl moiety. Complex 24 is to the best of our knowledge the first zwitterionic heteromultimetallic system set up by organometallic and metalorganic parts. For catalytic applications, two palladium complexes with hemilabile P/N ligands of type [Fe(η^5 - $C_5H_4PPh_2$)(η^5 - C_5H_4 terpy)] and [Fe(η^5 - $C_5H_4PPh_2$){ η^5 - C_5H_4 -CH=CHC(O)(py)}] were synthesized. They show good activity (TON = 160, TOF = 48 h^{-1}) as catalysts in the Heck-Mizoroki reaction [see reaction (2), Table 2, Figure 9] relative to $[PdCl_2(dppf)]$ [dppf = 1,1'-bis(diphenylphosphanyl)ferrocene]. However, catalysts reported by, for example, Fu et al.,^[30] Herrmann et al.,^[31] and Reetz et al.,^[32] are more active than 12 and 26 and can even be used for less-reactive aryl halides under mild conditions.

Experimental Section

General Data: All reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Tetrahydrofuran, toluene, *n*-hexane, and *n*-pentane were purified by distillation from sodium/benzophenone ketyl; dichloromethane and chloroform were purified by distillation from calcium hydride. Diethylamine and diisopropylamine were distilled from KOH; absolute methanol was obtained by distillation from magnesium.

Instruments: Infrared spectra were recorded with a Perkin–Elmer FTIR spectrometer Spectrum 1000. NMR spectra were recorded with a Bruker Avance 250 spectrometer [¹H NMR at 250.12 MHz and ¹³C(¹H) NMR at 62.86 MHz] in the Fourier transform mode. Chemical shifts are reported in δ units (parts per million) downfield



from tetramethylsilane ($\delta = 0.00$ ppm) with the solvent as the reference signal (CDCl₃: ¹H NMR, $\delta = 7.26$ ppm; ¹³C{¹H} NMR, $\delta = 77.16$ ppm).^[19] ³¹P{¹H} NMR spectra were recorded at 101.255 MHz in CDCl₃ with P(OMe)₃ as external standard [$\delta = 139.0$ ppm, relative to H₃PO₄ (85%) with $\delta = 0.00$ ppm]. ESI-TOF mass spectra were recorded with a Mariner biospectrometry workstation 4.0 (Applied Biosystems). Microanalyses were performed with a C,H,N-analyzer FlashAE 1112 (Thermo Company). Melting points of analytical pure samples (sealed off in nitrogenpurged capillaries) were determined with a Gallenkamp MFB 595010 M melting point apparatus.

Reagents: $[PdCl_2(cod)]$,^[33] $[PdBr_2(cod)]$,^[33] $[PtCl_2(SEt_2)_2]$,^[34] $[Mo-(CO)_4(nbd)]$,^[35] $[NiCl_2(dme)]$,^[36] [AuCl(tht)],^[37] $[{RhCl(cod)}_2]$,^[38] pyridylacetylpyridinium iodide,^[39] and 1-(diphenylphosphanyl)-1'-formylferrocene^[40] were prepared according to published procedures. All other chemicals were purchased from commercial suppliers and were used as received.

Synthesis of 3: Compound 1 (1.36 g, 3.34 mmol) was dissolved in dichloromethane (30 mL) and ethanol (150 mL). Acetylpyridine (2) (0.46 mL, 4.31 mmol) was added in a single portion to this mixture. After 5 min of stirring, an NaOH solution (12 mL, 2 M) was slowly dropped imto the reaction mixture. Stirring was continued for 2.5 h at 25 °C. The solution changed from orange to purple. The reaction mixture was evaporated to 50 mL and water (200 mL) was added. This solution was extracted twice with dichloromethane (200 mL potions). The organic phases were combined and dried with MgSO₄ and all volatile materials were removed in an oil-pump vacuum. The obtained crude material was purified by column chromatography on silica gel (column size: 4×15 cm, chloroform). With chloroform the starting material 1 could be eluted (100 mg, 0.25 mmol), whereas with ethyl acetate the title compound 3 was obtained. All volatiles were removed under reduced pressure. Compound 3 was isolated as a dark purple solid; yield 1.2 g (2.4 mmol, 70% based on 1). C₃₀H₂₄FeNOP (501.34): calcd. C 71.87, H 4.83, N 2.79; found C 71.60, H 5.05, N 2.71; m.p. 131 °C. IR (KBr): v = 1433 (m, v_{PC}), 1468 (m, v_{PC}), 1577 (s, $v_{C=C}$), 1594 (s, $v_{C=C}$), 1663 (s, v_{CO}) cm⁻¹. ¹H NMR (CDCl₃): δ = 4.14 (m, 2 H, C₅H₄), 4.38 (pt, J = 1.9 Hz, 2 H, C₅H₄), 4.40 (pt, J = 1.8 Hz, 2 H, C₅H₄), 4.56 (pt, J = 1.9 Hz, 2 H C₅H₄), 7.27–7.4 (m, 10 H, C₆H₅), 7.47 (ddd, ${}^{3}J = 7.6, 4.6 \text{ Hz}, {}^{4}J = 1.0 \text{ Hz}, 1 \text{ H}, \text{C}_{5}\text{H}_{4}\text{N}), 7.72 \text{ (d, } {}^{3}J = 15.8 \text{ Hz},$ 1 H, C₅H₄N), 7.77 (d, ${}^{3}J$ = 15.8 Hz, 1 H, C₅H₄N), 7.86 (ddd, ${}^{3}J$ = 7.6, 7.8 Hz, ${}^{4}J$ = 1.8 Hz, 1 H, C₅H₄N), 8.17 (ddd, ${}^{3}J$ = 7.8 Hz, ${}^{4}J$ = 1.0 Hz, ${}^{5}J$ = 0.9 Hz, 1 H, C₅H₄N), 8.73 (ddd, ${}^{3}J$ = 4.6 Hz, ${}^{4}J$ = 1.8 Hz, ${}^{5}J = 0.9$ Hz, 1 H, C₅H₄N) ppm. ${}^{13}C{}^{1}H$ NMR (CDCl₃): δ = 70.4 (C₅H₄), 73.0 (C₅H₄), 73.3 (d, ³J_{CP} = 4 Hz, C₅H₄), 74.4 (d, $^2J_{\rm CP}$ = 14 Hz, $Ci\text{-}{\rm C_5H_4}),$ 77.9 ($Ci\text{-}{\rm C_5H_4}),$ 80.3 (${\rm C_5H_4}),$ 118.8 (CO-CH=CH-), 123.0 (C₅H₄N), 126.7 (C₅H₄N), 128.4 (³J_{CP} = 7 Hz, m- C_6H_5), 128.8 (*p*- C_6H_5), 133.6 (d, ${}^2J_{CP}$ = 20 Hz, *o*- C_6H_5), 137.0 (C_5H_4N) , 138.8 (d, ${}^{1}J_{CP}$ = 10 Hz, *Ci*-C₆H₅), 146.4 (CO-CH=CH-), 148.9 (C₅H₄N), 154.8 (C₅H₄N), 188.6 (CO-CH=CH-) ppm. ³¹P{¹H} NMR (CDCl₃): δ = -18.5 ppm. ESI-TOF-MS: m/z = [M + H]⁺ 502.17.

Synthesis of 5: Compound 3 (2.9 g, 5.78 mmol), ammonium acetate (5.0 g, 64.87 mmol), and 4 (2.2 g, 6.93 mmol) were dissolved in degassed ethanol (20 mL) and heated for 3 h to reflux. An orange solid precipitated. The reaction mixture was allowed to cool to 25 °C. The orange solid was filtered off and washed twice with ice-cooled ethanol (25 mL portions); the residue was dried in an oil-pump vacuum; yield 1.67 g (2.77 mmol, 48% based on 3). $C_{37}H_{28}FeN_3P$ (601.46): calcd. C 73.89, H 4.69, N 6.99; found C 73.39, H 4.80, N 6.82; m.p. 186 °C. IR (KBr): $\tilde{v} = 1433$ (m, v_{PC}),

1468 (m, ν_{PC}), 1576 (s, ν_{C=C}), 1584 (s, ν_{C=C}), 1602 (s, ν_{C=C}) cm⁻¹. ¹H NMR (CDCl): δ = 4.06 (pq, *J* = 1.9 Hz, 2 H, C₅H₄), 4.24 (pt, *J* = 1.9 Hz, 2 H, C₅H₄), 4.34 (pt, *J* = 1.9 Hz, 2 H, C₅H₄), 4.88 (pt, *J* = 1.9 Hz, 2 H, C₅H₄), 7.26–7.4 (m, 12 H, C₆H₅/5-C₅H₄N), 7.88 (ddd, ³*J* = 7.9, 8.0 Hz, ⁴*J* = 1.8 Hz, 2 H, C₅H₄N), 8.46 (s, 2 H, C₅H₂N), 8.64 (ddd, ³*J* = 8 Hz, ⁴*J* = 1.0, ⁵*J* = 0.9 Hz, 2 H, C₅H₄N), 8.75 (ddd, ³*J* = 4.8 Hz, ⁴*J* = 1.8 Hz, ⁵*J* = 0.9 Hz, 2 H, C₅H₄N), ppm. ¹³C{¹H} NMR (CDCl₃): δ = 68.4 (C₅H₄), 71.8 (C₅H₄), 73.8 (d, ³*J*_{CP} = 4 Hz, C₅H₄), 74.5 (d, ²*J*_{CP} = 14 Hz, C₅H₄), 77.9 (*Ci*-C₅H₄), 82.4 (*Ci*-C₅H₄), 117.9 (3-C₅H₂N), 121.4 (C₅H₄N), 123.8 (C₅H₄N), 128.4 (d, ³*J*_{CP} = 7 Hz, *m*-C₆H₅), 128.8 (*p*-C₆H₅), 133.5 (d, ²*J*_{CP} = 20 Hz, *o*-C₆H₅), 138.9 (C₅H₄N), 139.2 (d, ¹*J*_{CP} = 10 Hz, *Ci*-C₆H₅), 149.1 (C₅H₄N), 150.1 (4-C₅H₂N), 156.5 (C₅H₄N), 158.1 (2-C₅H₂N) ppm. ³¹P{¹H} NMR (CDCl₃): δ = -18.3 ppm. ESI-MS: *m*/*z* = [M + H]⁺ 602.24.

Synthesis of 7: Compound 5 (200 mg, 0.33 mmol) dissolved in dichloromethane (25 mL) was slowly dropped into a solution of $[PtCl_2(SEt_2)_2]$ (6) (148.5 mg, 0.33 mmol) in dichloromethane (20 mL). After 10 min of stirring, the solvent was evaporated to 5 mL and diethyl ether (30 mL) was added. Compound 7 crystallized as orange needles at -30 °C. The crystals were washed with diethyl ether (40 mL) and dried in an oil-pump vacuum; yield 172 mg (0.18 mmol, 55% based on 5). C₄₁H₃₈Cl₂FeN₃PPtS (957.63): calcd. C 51.42, H 4.00, N 4.39; found C 51.50, H 3.82, N 4.39; m.p. 189.3 °C (dec.). IR (KBr): $\tilde{v} = 1435$ (m, v_{PC}), 1468 (m, v_{PC}), 1567 (s, $v_{C=C}$), 1583 (s, $v_{C=C}$), 1600 (s, $v_{C=C}$), 2928 (w, v_{CH}), 2966 (w, v_{CH}) cm⁻¹. ¹H NMR (CDCl₃): δ = 1.08 (t, ³J = 7.2 Hz 6 H, SCH₂CH₃), 2.50 (q, ${}^{3}J$ = 7.2 Hz 4 H, SCH₂CH₃), 4.32 (pq, J = 1.9 Hz, 2 H, C_5H_4), 4.35 (pt, J = 1.9 Hz, 2 H, C_5H_4), 4.70 (pt, J =1.8 Hz, 2 H, C₅H₄), 4.90 (pt, J = 1.8 Hz, 2 H, C₅H₄), 7.36 (ddd, ³J = 7.7, 1.2 Hz, ${}^{4}J$ = 1.2 Hz, 2 H, C₅H₄N), 7.4–7.7 (m, 12 H, C₆H₅/ 5-C₅H₄N), 7.88 (ddd, ${}^{3}J$ = 7.7, 7.8 Hz, ${}^{4}J$ = 1.8 Hz, 2 H, C₅H₄N), 8.46 (s, 2 H, C₅H₂N), 8.64 (ddd, ${}^{3}J$ = 7.8 Hz, ${}^{4}J$ = 1.2 Hz, ${}^{5}J$ = 0.9 Hz, 2 H, C₅H₄N), 8.75 (ddd, ${}^{3}J$ = 4.8 Hz, ${}^{4}J$ = 1.8 Hz, ${}^{5}J$ = 0.9 Hz, 2 H, C₅H₄N) ppm. ³¹P{¹H} NMR (CDCl₃): δ = 4.9 (J_{PPt} = 3690 Hz) ppm.

Synthesis of 9: Compound 5 (100 mg, 0.17 mmol) was dissolved in dichloromethane (10 mL), and [PtCl₂(SEt₂)₂] (6) (37 mg, 0.08 mmol) was added in a single portion. After 10 min of stirring, the reaction solution was evaporated to 5 mL and n-hexane (30 mL) was added. Molecule 9 crystallized as orange needles at -30 °C. The crystals were washed with *n*-hexane (40 mL) and dried in an oil-pump vacuum; yield 108 mg (0.073 mmol, 89% based on 5). C74H56Cl2Fe2N6P2Pt (0.5 C6H14) (1511.99): calcd. C 61.17, H 4.20, N 5.56; found C 61.07, H 4.43, N 5.18; m.p. 153 $^{\circ}\mathrm{C}$ (dec.). IR (KBr): $\tilde{v} = 1439$ (m, v_{PC}), 1468 (m, v_{PC}), 1567 (s, $v_{C=C}$), 1584 (s, $v_{C=C}$), 1602 (s, $v_{C=C}$) cm⁻¹. ¹H NMR (CDCl₃): δ = 4.22 (m, 4 H, C₅H₄), 4.61 (m, 4 H, C₅H₄), 4.91 (m, 4 H, C₅H₄), 5.08 (m, 4 H, C_5H_4), 7.33 (ddd, ${}^{3}J$ = 7.9, 4.8 Hz, ${}^{4}J$ = 1.0 Hz, 4 H, C_5H_4N), 7.38– 7.7 (m, 24 H, C₆H₅/5-C₅H₄N), 7.86 (ddd, ${}^{3}J$ = 7.9, 8.0 Hz, ${}^{4}J$ = 1.8 Hz, 4 H, C_5H_4N), 8.47 (s, 4 H, C_5H_2N), 8.62 (ddd, ${}^{3}J$ = 8 Hz, ${}^{4}J = 1.0 \text{ Hz}, {}^{5}J = 0.9 \text{ Hz}, 4 \text{ H}, \text{ C}_{5}\text{H}_{4}\text{N}), 8.73 \text{ (ddd, } {}^{3}J = 4.8 \text{ Hz},$ ${}^{4}J = 1.8 \text{ Hz}, {}^{5}J = 0.9 \text{ Hz}, 4 \text{ H}, \text{ C}_{5}\text{H}_{4}\text{N} \text{ ppm}. {}^{31}\text{P}{}^{1}\text{H} \text{ NMR}$ (CDCl₃): δ = 10.0 (J_{PPt} = 2629 Hz) ppm. ESI-MS: m/z = $[M + H]^+$ 1469.90.

Synthesis of 12: Compound 5 (500 mg, 0.83 mmol) was dissolved in dichloromethane (25 mL) and $[PdCl_2(cod)]$ (11a) (237 mg, 0.83 mmol) was added in a single portion at 25 °C. After 30 min of being stirred in the dark, the solution was filtered through Celite and the filtrate was evaporated to 5 mL. The product precipitated by addition of diethyl ether (30 mL). The solid was filtered off, washed twice with *n*-hexane (20 mL), and dried in an oil-pump vacuum; yield 485 mg (0.62 mmol, 74% based on 5). C₃₇H₂₈Cl₂FeN₃PPd (0.5 CH₂Cl₂) (821.25): calcd. C 55.17, H 3.53, N 5.08; found C 55.47, H 3.62, N 4.97; m.p. 188 °C (dec.). IR (KBr): $\tilde{v} = 1434$ (m, v_{PC}), 1471 (m, v_{PC}), 1585 (s, $v_{C=C}$), 1595 (s, $v_{C=C}$ cm⁻¹. ¹H NMR (CDCl₃): δ = 4.32 (br. s, 2 H, C₅H₄), 4.66 (br. s, 2 H, C_5H_4), 4.7 (pt, J = 1.8 Hz, 2 H, C_5H_4), 5.30 (s, 1 H, CH₂Cl₂) 5.77 (br. s, 2 H, C₅H₄), 7.3–7.51 (m, 8 H, C₆H₅/C₅H₄N), 7.55–7.66 (m, 4 H, C₆H₅), 7.83 (ddd, ${}^{3}J$ = 7.9, 7.8 Hz, ${}^{4}J$ = 1.8 Hz, 1 H, C₅H₄N), 7.95 (ddd, ${}^{3}J$ = 7.9, 7.8 Hz, ${}^{4}J$ = 2.0 Hz, 1 H, C₅H₄N-Pd), 8.37 (ddd, ${}^{3}J = 7.8$ Hz, ${}^{4}J = 1$ Hz, ${}^{5}J = 0.8$ Hz, 1 H, C₅H₄N-Pd), 8.61 (d, ${}^{4}J$ = 1.3 Hz, 1 H, C₅H₂N), 8.63 (ddd, ${}^{3}J$ = 7.8 Hz, ${}^{4}J$ = 1 Hz, ${}^{5}J$ = 1 Hz, 1 H, C₅H₄N), 8.74 (ddd, ${}^{3}J$ = 4.8 Hz, ${}^{4}J$ = 1.8 Hz, ${}^{5}J = 0.8$ Hz, 1 H, C₅H₄N), 9.04 (ddd, ${}^{3}J = 3.7$ Hz, ${}^{4}J =$ 2 Hz, ${}^{5}J = 1 \text{ Hz}$, 1 H, C₅H₄N-Pd), 10.46 (d, ${}^{4}J = 1.3 \text{ Hz}$, 1 H, C_5H_2N) ppm. ³¹P{¹H} NMR (CDCl₃): δ = 23.5 ppm. ESI-TOF-MS: $m/z = [M + H]^+$ 780.05.

Synthesis of 14: Compound 12 (100 mg, 0.13 mmol) was dissolved in tetrahydrofuran (50 mL) and [NiCl₂(dme)] (13) (28.3 mg, 0.13 mmol) was added in a single portion. After a few seconds, a red solid started to precipitate. The solid was filtered off and washed twice with diethyl ether. After drying the precipitate in an oil-pump vacuum it was dissolved in dimethyl sulfoxide (10 mL). Next, *n*-hexane (40 mL) was added, at which point 14 precipitated in the form of red crystals that were washed twice with *n*-hexane (30 mL); yield 112 mg (0.107 mmol, 81% based on 12). $C_{41}H_{40}Cl_4FeN_3NiO_2PPdS_2$ (1064.65): calcd. C 46.25, H 3.79, N 3.96; found C 46.52, H 3.65, N 4.05. Mp. 215 °C (dec.). IR (KBr): $\tilde{v} = 1432$ (m, v_{PC}), 1472 (m, v_{PC}), 1547 (s, $v_{C=C}$), 1570 (s, $v_{C=C}$), 1602 (s, $v_{C=C}$) cm⁻¹.

Synthesis of 16a: Compound **16a** was prepared as described for the synthesis of **9**. Instead of [PtCl₂(SEt₂)₂] (**6**), [PdCl₂(cod)] (**11a**) (23 mg, 0.08 mmol) was used; yield 96 mg (0.07 mmol, 84% based on **5**); m.p. 140 °C (dec.). IR (KBr): $\tilde{v} = 1438$ (m, v_{PC}), 1467 (m), 15767 (s, $v_{C=C}$), 1584 (s, $v_{C=C}$), 1602 (s, $v_{C=C}$) cm⁻¹. ¹H NMR (250 MHz, CDCl₃): $\delta = 4.23$ (m, 4 H, C₅H₄), 4.64 (m, 4 H, C₅H₄), 4.91 (m, 4 H, C₅H₄), 5.00 (m, 4 H, C₅H₄), 7.26–7.7 (m, 24 H, C₆H₅/C₅H₄N), 7.86 (ddd, ³J = 7.9, 8.0 Hz, ⁴J = 1.8 Hz, 4 H, C₅H₄N), 8.47 (s, 4 H, C₅H₄N), 8.62 (ddd, ³J = 8 Hz, ⁴J = 1.0 Hz, ⁵J = 0.9 Hz, 4 H, C₅H₄N) ppm. ³¹P{¹H} NMR (CDCl₃): $\delta = 14.3$ ppm. ESI-MS: $m/z = [M + H]^+$ 1379.24.

Synthesis of 16b: Compound **16b** was prepared as described for the synthesis of **9**. Instead of [PtCl₂(SEt₂)₂] (**6**), [PdBr₂(cod)] (**11b**) (30 mg, 0.08 mmol) was used; yield 103 mg (0.07 mmol, 84% based on **5**). $C_{74}H_{56}Br_2Fe_2N_6P_2Pd$ (0.5 C_6H_{14}) (1509.07): calcd. C 61.16, H 4.20, N 5.56; found C 61.10, H 4.39, N 5.35; m.p. 240 °C (dec.). IR (KBr): $\tilde{v} = 1467$ (s, v_{PC}), 1533 (m, $v_{C=C}$) cm⁻¹. ¹H NMR (CDCl₃): $\delta = 4.27$ (pt, J = 1.8 Hz, 4 H, C_5H_4), 4.63 (pt, J = 1.8 Hz, 4 H, C_5H_4), 4.37 (pt, J = 1.8 Hz, 4 H, C_5H_4), 5.07 (pt, J = 1.8 Hz, 4 H, C_5H_4 N), 7.87 (dt, ³J = 7.5, 3.0 Hz, 4 H, C_5H_4 N), 8.49 (s, 4 H, C_5H_4 N), 8.62 (d, ³J = 3.0 Hz, 4 H, C_5H_4 N), 8.75 (d, ³J = 4.79 Hz, 4 H, C_5H_4 N) ppm. ³¹P{¹H} NMR (CDCl₃): $\delta = 13.4$ ppm. ESI-MS: $m/z = [M + K]^+$ 1507.03.

Synthesis of 17: Compound **17** was prepared as described for **9**. Instead of $[PtCl_2(SEt_2)_2]$ **(6)**, $[Mo(CO)_4(nbd)]$ **(15)** (24 mg, 0.08 mmol) was used; yield 68 mg (0.05 mmol, 59% based on **5**); m.p. 153 °C (dec.). IR (KBr): $\tilde{v} = 1438$ (m, v_{PC}), 1468 (m, v_{PC}), 1567 (s, $v_{C=C}$), 1584 (s, $v_{C=C}$), 1602 (s, $v_{C=C}$), 1812 (s, v_{CO}), 1867 (s, v_{CO}), 1900 (s, v_{CO}), 2018 (s, v_{CO}) cm⁻¹. ¹H NMR (CDCl₃): $\delta = 4.07$ (m, 4 H, C₅H₄), 4.12 (m, 4 H, C₅H₄), 4.21 (pt, J = 1.8 Hz, 4 H,



C₅H₄), 4.63 (pt, J = 1.8 Hz, 4 H, C₅H₄), 7.17–7.24 (m, 20 H, C₆H₅), 7.34 (ddd, ${}^{3}J = 7.5$, 4.7 Hz, ${}^{4}J = 1$ Hz, 4 H, C₅H₄N), 7.86 (ddd, ${}^{3}J = 7.5$, 7.9 Hz, ${}^{4}J = 1.8$ Hz, 4 H, C₅H₄N), 8.33 (s, 4 H, C₅H₂N), 8.61 (ddd, ${}^{3}J = 7.9$ Hz, ${}^{4}J = 1$ Hz, ${}^{5}J = 0.8$ Hz, 4 H, C₅H₄N), 8.73 (ddd, ${}^{3}J = 4.7$ Hz, ${}^{4}J = 1.8$ Hz, ${}^{5}J = 0.8$ Hz, 4 H, C₅H₄N) ppm. ${}^{31}P{^{1}H}$ NMR (CDCl₃): $\delta = 25.9$ ppm. ESI-MS: $m/z = [M + H]^{+}$ 1411.20.

Synthesis of [{CuBr(5)}_n] (19): Compound 5 (100 mg, 0.17 mmol) was dissolved in tetrahydrofuran (20 mL) and [CuBr] (18) (24 mg, 0.17 mmol) was added in a single portion. After two hours of stirring at 25 °C, the [CuBr] had been consumed and the solution was evaporated to 5 mL. Next n-hexane (30 mL) was added, at which point a red-orange material precipitated. The solid was filtered off and washed twice with n-hexane (30 mL portions) and was then dried in an oil-pump vacuum; yield 120 mg (0.16 mmol, 95% based on 5). C₃₇H₂₈BrCuFeN₃P (744.91): calcd. C 59.66, H 3.79, N 5.64; found C 59.16, H 4.02, N 5.49; m.p. 180 °C (dec.). IR (KBr): v = 1473 (s, v_{PC}), 1535 (m, $v_{C=C}$) cm⁻¹. ¹H NMR (CDCl₃): δ = 4.21 (pt, J = 1.8 Hz, 2 H, C₅H₄), 4.37 (pt, J = 1.8 Hz, 2 H, C₅H₄), 4.43 (pt, J = 1.9 Hz, 2 H, C₅H₄), 4.36 (pt, J = 1.9 Hz, 2 H, C₅H₄), 7.13– 7.32 (m, 12 H, C_6H_5/C_5H_4N), 7.83 (pt, ${}^{3}J$ = 7.9 Hz, 2 H, C_5H_4N), 8.53 (s, 2 H, C_5H_4N), 8.64 (d, ${}^{3}J$ = 7.9 Hz, 2 H, C_5H_4N), 8.32 (d, ${}^{3}J = 4.33 \text{ Hz}, 2 \text{ H}, \text{ C}_{5}\text{H}_{4}\text{N}$ ppm. ${}^{31}\text{P}\{{}^{1}\text{H}\}$ NMR (CDCl₃): $\delta =$ -14.9 ppm. ESI-MS: $m/z = [M - Br]^+ 664.13$.

Synthesis of 22: Compound **22** was prepared as described for the synthesis of **19**. In this respect [AuCl(tht)] (**20**) (55 mg, 0.17 mmol) was used; yield 131 mg (0.16 mmol, 93% based on **5**.). $C_{37}H_{28}AuClFeN_3P(C_6H_{14})$ (920.05): calcd. C 56.13, H 4.60, N 4.57; found C 55.92, H 4.43, N 4.35; m.p. 135 °C (dec.). IR (KBr): $\tilde{v} = 1471$ (s, v_{PC}), 1531 (m, $v_{C=C}$) cm⁻¹. ¹H NMR (CDCl₃): $\delta = 4.36$ (pt, J = 1.8 Hz, 2 H, C_5H_4), 4.42 (pt, J = 1.8 Hz, 2 H, C_5H_4), 4.59 (pt, J = 1.9 Hz, 2 H, C_5H_4), 4.91 (pt, J = 1.9 Hz, 2 H, C_5H_4), 7.30–7.47 (m, 10 H, C_6H_5), 7.55 (ddd, ³J = 7.40 Hz, ³J = 4.9 Hz, 2 H, C_5H_4 N), 7.87 (dt, ³J = 7.40, 3.0 Hz, 2 H, C_5H_4 N), 8.35 (s, 2 H, C_5H_2 N), 9.62 (d, ³J = 7.9 Hz, 2 H, C_5H_4 N), 9.75 (dd, ³J = 4.9 Hz, ⁴J = 1.3 Hz, 2 H, C_5H_4 N) ppm. ³¹P{¹H} NMR (CDCl₃): $\delta = 27.2$ ppm. ESI-MS: $m/z = [M - Cl]^+$ 798.14.

Synthesis of 23: Compound **23** was prepared as described for the synthesis of **19.** In this case, $[\{RhCl(cod)\}_2]$ **(21)** (42 mg, 0.09 mmol) was used; yield 137 mg, 0.16 mmol, 95% based on **5**; m.p. 194 °C (dec.). IR (KBr): $\tilde{v} = 1473$ (s, v_{PC}), 1535 (m, $v_{C=C}$) cm^{-1.} ¹H NMR (CDCl₃): $\delta = 2.40$ (m, 8 H, cod), 4.28 (pt, J = 1.8 Hz, 2 H, C₅H₄), 4.69 (pt, J = 1.8 Hz, 2 H, C₅H₄), 4.74 (pt, J = 1.9 Hz, 2 H, C₅H₄), 5.15 (pt, J = 1.9 Hz, 2 H, C₅H₄), 5.60 (s, 4 H, cod), 7.25-7.31 (m, 10 H, C₆H₅), 7.54 (dpt, ³J = 8.00 Hz, ⁴J = 2.0 Hz, 2 H, C₅H₄N), 7.83 (ddd, ³J = 7.90 Hz, ⁴J = 1.9 Hz, 2 H, C₅H₄N), 8.55 (s, 2 H, C₅H₂N), 8.66 (d, ³J = 3.0 Hz, 2 H, C₅H₄N), 8.73 (dd, ³J = 4.30 Hz, ⁴J = 1.8 Hz, 2 H, C₅H₄N) ppm. ³¹P{¹H} NMR (CDCl₃): $\delta = 22.1$ (d, $J_{Rh,P} = 151$ Hz) ppm. ESI-MS: $m/z = [M - cod]^+$ 739.07, [M]⁺ 847.21.

Synthesis of 25: Compound 22 (300 mg, 0.36 mmol) was dissolved in ethanol (50 mL) and [RuCl₂(dmso)₄] (24) (87 mg, 0.18 mmol) was added in a single portion. The reaction mixture was heated to reflux for 12 h. After removing all volatiles in an oil-pump vacuum, the remaining solid was washed five times with *n*-hexane (10 mL portions) and dried in vacuo; yield 315 mg (0.17 mmol, 95% based on 22). $C_{74}H_{56}Au_2Cl_4Fe_2N_6P_2Ru$ (1839.73): calcd. C 48.31, H 3.07, N 4.57; found C 48.66, H 3.21, N 4.38%; m.p. 245 °C (dec.). IR (KBr): $\tilde{v} = 1431$ (m, v_{PC}), 1609 (s, $v_{C=C}$) cm⁻¹. ¹H NMR (CDCl₃): $\delta = 4.21$ (pt, J = 1.8 Hz, 4 H, C_5H_4), 4.43 (pt, J = 1.8 Hz, 4 H, C₅H₄), 5.29 (pt, J = 1.9 Hz, 4 H, C₅H₄), 5.43 (pt, J = 1.9 Hz, 4 H, C₅H₄), 7.06–7.43 (m, 20 H, C₆H₅), 7.54 (m, 4 H, C₅H₄N), 8.63 (dt, ³J = 7.9 Hz, ³J = 3.0 Hz, 4 H, C₅H₄N), 9.46 (d, ³J = 3.0 Hz, 4 H, C₅H₄N), 9.53 (dd, ³J = 4.30 Hz, ⁴J = 1.8 Hz, 4 H, C₅H₄N), 9.67 (s, 4 H, C₅H₂N) ppm. ³¹P{¹H} NMR (CDCl₃): $\delta = 27.4$ ppm.

Synthesis of 26: Compound 3 (500 mg, 1.0 mmol) was dissolved in dichloromethane (25 mL) and [PdCl₂(cod)] (11a) (285 mg, 1.0 mmol) was added in a single portion. After 20 min of stirring, the reaction mixture was evaporated to 5 mL and diethyl ether (30 mL) was added. A purple solid precipitated and was filtered off. The solid was washed twice with n-hexane (10 mL) and dried in an oil-pump vacuum; yield 612 mg (0.9 mmol, 90% based on 3). C₃₀H₂₄Cl₂FeNOPPd·(0.5 CH₂Cl₂·H₂O) (730.14): calcd. C 50.17, H 3.59, N 1.92; found C 50.14, H 3.58, N 1.88; m.p. 215 °C (dec.). IR (KBr): $\tilde{v} = 1435$ (m, v_{PC}), 1481 (m, v_{PC}), 1586 (s, $v_{C=C}$), 1602 (s, $v_{C=C}$), 1667 (s, v_{CO}) cm⁻¹. ¹H NMR (CDCl₃): δ = 4.63 (m, 2 H, C₅H₄), 4.74 (m, 2 H, C₅H₄), 4.83 (m, 2 H, C₅H₄), 5.30 (s, 1 H, CH₂Cl₂), 5.38 (m, 2 H, C₅H₄), 7.3–7.68 (m, 10 H, C₆H₅), 7.63 (m, 1 H, C₅H₄N), 7.94 (m, 1 H, C₅H₄N), 7.95 (d, ${}^{3}J$ = 15.8 Hz, 1 H, CO-CH=CH), 8.01 (d, ${}^{3}J$ = 15.8 Hz, 1 H, CO-CH=CH), 8.84 (m, 1 H, C₅H₄N), 9.0 (m, 1 H, C₅H₄N) ppm. ¹³C{¹H} NMR (CDCl₃): $\delta = 68.1 \text{ (C}_5\text{H}_4\text{)}, 69.7 \text{ (C}_5\text{H}_4\text{)}, 70.8 \text{ (d, } {}^3J_{\text{C},\text{P}} = 4 \text{ Hz}, \text{ C}_5\text{H}_4\text{)}, 72.8 \text{ (d, }$ ${}^{2}J_{C,P} = 14 \text{ Hz}, C_{5}H_{4}), 76.3 (Ci-C_{5}H_{4}), 81.5 (C_{i}-C_{5}H_{4}), 122.3 (CO-C_{5}H_{4}), 12$ CH=CH), 125.5 (C₅H₄N), 127.2 (C₅H₄N), 128.9 (d, ${}^{3}J_{C,P}$ = 7 Hz, C_6H_5), 131.1 (C_6H_5), 134.0 (d, ${}^2J_{C,P}$ = 20 Hz, C_6H_5), 139.1 (C₅H₄N), 144.8 (CO-CH=CH), 151.2 (d, ${}^{1}J_{C,P} = 10$ Hz, Ci-C₆H₅), 151.4 (C₅H₄N), 156.9 (C₅H₄N), 188.2 (CO-CH=CH) ppm. ³¹P{¹H} NMR (CDCl₃): δ = 22.1 ppm. ESI-MS: $m/z = [M + H]^+$ 678.08.

Heck–Mizoroki Reaction of Iodobenzene (27) with *tert*-Butyl Acrylate (28): Iodobenzene (654 mg, 5.1 mmol), *tert*-butyl acrylate (672 mg, 5.2 mmol), $EtNiPr_2$ (672 mg, 5.2 mmol), and acetylferrocene (114 mg, 0.5 mmol) were dissolved in a toluene/acetonitrile mixture [20 mL, ratio 1:1 (v/v)] and loaded with 0.5 mol-% of the respective catalyst (12, 26, or 30). [CuI] (2 equiv.) was added in a single portion. The reaction suspension was stirred at 80 °C. Samples (1 mL) were taken every hour over a period of 9 h. An additional sample was taken after 25 h. The samples were subjected to chromatography on silica gel with diethyl ether as eluent. All volatiles were evaporated from the samples under reduced pressure. The conversions were determined by ¹H NMR spectroscopy with acetylferrocene as an internal standard.

Crystal data for **5**, **9**, **12**, **14**, **16b**, **22**, and **26** are presented in Table 3 (**5**, **9**, **12**, **14**) and Table 4 (**16b**, **22**, **26**). The data for **12**, **14**, and **26** were collected with an Oxford Gemini S diffractometer, whereas the data for **5**, **9**, **16b**, and **22** were collected with a Bruker Smart 1K CCD diffractometer with graphite-monochromatized Mo- K_a ($\lambda = 0.71073$ Å) for **5**, **9**, **12**, **16b**, **22**, and **26** or Cu- K_a radiation ($\lambda = 1.54184$ Å) for molecule **14** using oil-coated shock-cooled crystals. The structures were solved by direct methods using SHELXS-97^[41] or SIR-92^[42] and refined by full-matrix least-squares procedures on F^2 using SHELXL-97.^[43] All non-hydrogen atoms were refined anisotropically and a riding model was employed in the refinement of the hydrogen atom positions.

CCDC-775761 (for 5), -775762 (for 9), -775763 (for 12), -775764 (for 14), -775765 (for 16b), -775766 (for 22), and -775767 (for 26) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/ data_request/cif.

	5	9	12	14
Formula weight	601.44	1468.88	850.85	1234.46
Chemical formula	C ₃₇ H ₂₈ FeN ₃ P	$C_{74}H_{56}Cl_2Fe_2N_6P_2Pt$	C ₄₁ H ₃₆ Cl ₂ FeN ₃ OPPd	C43H44Cl8FeN3NiOPPdS2
Crystal system	tetragonalic	monoclinic	monoclinic	monoclinic
Space group	$P4_2/n$	$P2_1/c$	$P2_1/c$	$P2_{1}/c$
<i>a</i> [Å]	27.667(10)	13.113(4)	14.5568(7)	15.6337(7)
b [Å]	27.667(10)	17.246(4)	20.0956(6)	12.9595(3)
c [Å]	7.751(5)	14.707(5)	14.6087(6)	25.0932(2)
	90	90	90	90
β[°]	90	110.954(10)	116.427(5)	95.5010(10)
γ [°]	90	90	90	90
V[Å ³]	5933(5)	3106.0(15)	3826.9(3)	5060.59(14)
$\rho_{\rm calcd.} [\rm gcm^{-3}]$	1.347	1.571	1.477	1.620
F(000)	2496	1472	1728	2488
Crystal size [mm]	$0.3 \times 0.03 \times 0.02$	$0.2 \times 0.2 \times 0.1$	$0.6 \times 0.5 \times 0.3$	$0.3 \times 0.1 \times 0.1$
Z	8	2	4	4
Index ranges	$-23 \le h \le 23$	$-16 \le h \le 15$	$-17 \le h \le 17$	$-17 \le h \le 17$
-	$0 \le k \le 33$	$0 \le k \le 21$	$-24 \le k \le 24$	$-14 \le k \le 13$
	$0 \le l \le 9$	$0 \le l \le 18$	$-18 \le l \le 18$	$-28 \le l \le 28$
$\mu \text{ [mm^{-1}]}$	0.594	2.895	1.066	10.807
<i>T</i> [K]	298	298	100	100
θ [°]	1.47 to 25.35	1.66 to 26.38	2.97 to 26.00	3.20 to 60.69
Total reflections	25251	34416	34308	35666
Unique reflections	6524	6598	7352	7547
$R_{\rm int} [\%]^{[a]}$	7.04	4.45	2.55	3.83
Data/restraints/parameters	5441/0/380	6359/0/394	7352/122/497	7547/66/615
$R_1,^{[a]} w R_2^{[a]} [I \ge \sigma(I)]$	0.0664, 0.1719	0.0279, 0.0521	0.0663, 0.1762	0.0670, 0.1931
$R_{1}^{[a]} w R_{2}^{[a]}$ (all data)	0.1393, 0.2299	0.0427, 0.0589	0.0778, 0.1831	0.0962, 0.2201
Godness-of-fit on $F^{2[b]}$	1.040	1.148	1.193	1.157
$\Delta \rho \ [e Å^{-3}]$	0.405, -0.434	0.859, -0.811	3.103, -1.414	2.446, -1.902

[a] $R = [\Sigma(||F_o| - |F_c||)/\Sigma|F_o|]/\Sigma|F_o|; wR_2 = {\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma(wF_o^4)}^{\frac{1}{2}}. w = 1/[\sigma^2(F_o^2) + (0.0835P)^2 + 4.1728P], P = (F_o^2 + 2F_c^2)/3.$ [b] $S = [\Sigma w(F_o^2 - F_c^2)^2]/(n-p)^{\frac{1}{2}}. (n = number of reflections, p = parameters used).$

-1 $(1/10)$ -1 , $\times/1$ you $(1/10)$	Table 4.	Crystal	and	intensity	collection	data	for	16b.	22.	and 26.
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	16b	22	26
Formula weight	1469.11	833.85	689.43
Chemical formula	$C_{74}H_{56}Br_2Fe_2N_6P_2Pd$	C ₃₇ H ₂₈ AuClFeN ₃ P	$C_{30}H_{25,20}Cl_2FeNO_{1.60}PPd$
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_{1}/c$	$P\overline{1}$	$P\overline{1}$
a [Å]	12.879(3)	9.9416(14)	10.1183(9)
b [Å]	17.208(5)	12.6191(18)	11.1906(8)
c [Å]	14.573(4)	13.860(2)	13.5351(10)
	90	112.005(2)	90.340(6)
β[°]	110.185(4)	101.591(2)	99.045(7)
γ [°]	14.573(4)	91.244(2)	113.162(7)
$V[Å^3]$	3031.5(14)	1570.2(4)	1387.64(19)
$\rho_{\text{caled}} [\text{g cm}^{-3}]$	1.609	1.764	1.650
F(000)	1480	816	692
Crystal size [mm]	$0.3 \times 0.1 \times 0.1$	$0.3 \times 0.2 \times 0.2$	$0.4 \times 0.3 \times 0.2$
Z	2	2	2
Index ranges	$-16 \le h \le 15$	$-12 \le h \le 12$	$-12 \le h \le 12$
-	$0 \le k \le 21$	$-15 \le k \le 15$	$-13 \le k \le 13$
	$0 \le l \le 188$	$-17 \le l \le 17$	$-16 \le l \le 16$
$\mu [{\rm mm}^{-1}]$	2.188	5.296	1.448
T[K]	298	298	100
θ[°]	1.68 to 26.46	1.63 to 26.41	2.91 to 26.05
Total reflections	21852	17961	13913
Unique reflections	6505	6400	5483
$R_{\rm int} [\%]^{(a)}$	7.72	2.81	1.11
Data/restraints/parameters	6171/0/394	6400/0/397	5483/0/351
$R_1,^{[a]} w R_2^{[a]} [I \ge \sigma(I)]$	0.0826, 0.2113	0.0217, 0.0519	0.0165, 0.0408
R_{1} , ^[a] wR_{2} ^[a] (all data)	0.1081, 0.2393	0.0282, 0.0544	0.0196, 0.0429
Godness-of-fit on $F^{2[b]}$	1.054	1.020	1.063
$\Delta \rho \ [e \text{\AA}^{-3}]$	2.771, -3.241	0.543, -0.597	0.442, -0.309

[a] $R = [\Sigma(||F_o| - |F_c||)/\Sigma|F_o|]/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma(wF_o^4)\}^{\frac{1}{2}}$. $w = 1/[\sigma^2(F_o^2) + (0.0835P)^2 + 4.1728P]$, $P = (F_o^2 + 2F_c^2)/3$. [b] $S = [\Sigma w(F_o^2 - F_c^2)^2]/(n - p)^{\frac{1}{2}}$ (*n* = number of reflections, *p* = parameters used).

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