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Transfer of heterocyclic carbene ligands from chromium to gold, palladium and platinum

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Abstract

The reaction of pentacarbonyl(pyrazolin-3-ylidene)chromium complexes, $[(CO)_5Cr\{\overline{CN(Me)N(Me)C(R)=CH}\}$ (**2a–c**) (R = Ph (**a**), $C_6H_4NMe_2$-4 (**b**); (C_5H_4)FeCp (**c**)), with $[AuCl(SMe_2)]$, $H[AuCl_4]$, $[PdCl_2(NCPh)_2]$ and $[PtCl_2(NCPh)_2]$ gives, by transfer of the heterocyclic carbene ligand, new chloro pyrazolin-3-ylidene complexes of gold(I) and gold(III), dichloro bis(pyrazolin-3-ylidene) palladium and dichloro bis(pyrazolin-3-ylidene) platinum in high yield. The chloride ligand in $[AuCl\{\overline{CN(Me)N(Me)C(Fc)=CH}\}]$ (Fc = (C_5H_4)FeCp) is readily displaced by trifluoroacetate. The analogous substitution of iodide for the chloride ligands in $[MCl_2\{\overline{CN(Me)N(Me)C(Fc)=CH}\}_2]$ (M = Pd, Pt) give the corresponding diiodo complexes although in a much slower reaction. In contrast, the reaction of silver trifluoroacetate with $[MCl_2\{\overline{CN(Me)N(Me)C(Fc)=CH}\}_2]$ affords a binuclear Pd–Ag complex containing two pyrazolin-3-ylidene and three trifluoroacetate ligands two of whom occupy bridging positions between Pd and Ag. The reactions of the pyrazolidin-3-ylidene complex $[(CO)_5Cr\{\overline{CN(Me)N(Me)C(R)_2CH_2}\}]$ (R = $C_6H_4NMe_2$-4) with $[AuCl(SMe_2)]$ and $[PdCl_2(NCPh)_2]$ yield chloro pyrazolidin-3-ylidene gold and dichloro bis(pyrazolidin-3-ylidene) palladium complexes. The related dichloro bis(tetrahydropyrimidin-4-ylidene) palladium complex is formed in the reaction of $[(CO)_5Cr\{\overline{CN(Me)CH_2N(Me)CPh=CH}\}]$ with the palladium complex $[PdCl_2(NCPh)_2]$. The solid-state structures of several of these heterocyclic carbene complexes including the structure of the binuclear Pd–Ag complex are established by X-ray structure analyses.

Keywords: Carbene complexes; Pyrazolin-3-ylidene complexes; Pyrazolidin-3-ylidene complexes; Transmetallation; Tetrahydropyrimidinylidene complexes

1. Introduction

Since the first isolation of a stable *N*-heterocyclic carbene (NHC) in 1991 [1], numerous stable NHCs have been prepared. In recent years *N*-heterocyclic carbenes have evolved into very powerful co-ligands for transition metal complexes that are active homogeneous catalysts [2]. *N*-Heterocyclic carbenes are increasingly replacing the traditional phosphane ligands especially in homogeneous catalysts that are used in cross-coupling reactions due to their strong σ-donating properties [3] and their low sensitivity to air and moisture. Until now the vast majority of syntheses and reactivity studies of NHC complexes were concerned with compounds containing imidazolin-2-ylidene and imidazolidin-2-ylidene complexes. Only recently, the reactivity and the catalytic activity of complexes with other heterocyclic [4] and even carbocyclic carbene ligands [5] have also gained some attention. Only few complexes containing a pyrazolin-3-ylidene ligand are known although in a recent theoretical investigation it has been shown that pyrazolin-3-ylidene ligands are even stronger σ-donors than imidazolin-2-ylidene ligands [6]. In addition to pentacarbonyl

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(1,2-dimethylpyrazolin-3-ylidene)chromium [6] and molybdenum [7] and the corresponding tetracarbonylbis(1,2-dimethylpyrazolin-3-ylidene) molybdenum [7] the synthesis of a few complexes of iron [8], copper [9], palladium [10] and rhodium [10,11] has been reported.

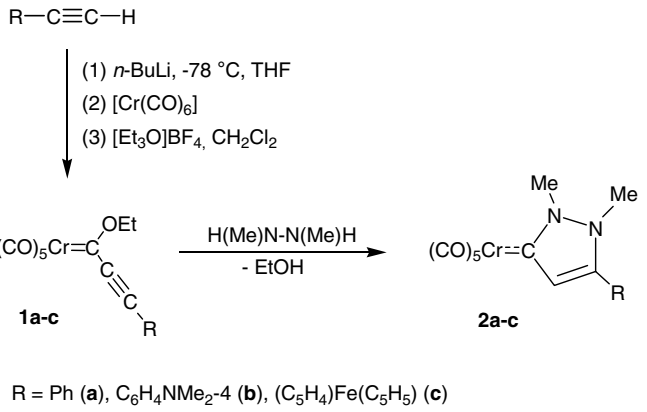
Usually NHC ligands are introduced into transition metal complexes starting from either the free carbene or suitable precursors [12]. Another approach is the stoichiometric transfer of carbene ligands from one metal to another (transmetallation) [13]. The first *photochemically* induced transfer of a Fischer-type carbene ligand (from molybdenum to iron and nickel) was reported by Fischer and Beck in 1970 [14]. Since then the carbene ligand in pentacarbonyl carbene complexes of chromium, molybdenum or tungsten has also *thermally* been transferred to other metals such as gold [15–17], cobalt [18], rhodium [16,17,19], palladium [16,17,20], platinum [16,17], copper [16,21] and silver [18]. Such transmetallations offer ready access to transition metal carbene complexes that cannot be prepared or are only difficult to obtain by conventional synthetic methods. We now report on the synthesis of pyrazolin-3-ylidene complexes via transfer of the pyrazolin-3-ylidene ligand from chromium to gold, palladium and platinum, the transfer of a pyrazolidin-3-ylidene ligand from chromium to gold and palladium, and on a brief and tentative evaluation of the catalytic activity of the palladium pyrazolin-3-ylidene complexes in C–C coupling reactions (Mizoroki–Heck and Suzuki–Miyaura reactions).

2. Results and discussion

2.1. Synthesis of the NHC chromium complexes

The pyrazolin-3-ylidene complexes were prepared from terminal alkynes, hexacarbonyl chromium, triethyloxonium tetrafluoroborate and 1,2-dimethylhydrazine. Deprotonation of the terminal alkynes phenylacetylene, 4-dimethylaminophenylacetylene and ethinylferrocene with *n*-butyllithium at −78 °C and subsequent reaction with hexacarbonyl chromium followed by alkylation of the resulting metallate with triethyloxonium tetrafluoroborate gave the alkynyl(ethoxy)carbene complexes **1a** [22], **1b** and **1c** [23]. Addition of 1,2-dimethylhydrazine (*in situ* generated from commercially available 1,2-dimethylhydrazine dihydrochloride and concentrated NaOH) to solutions of **1a–c** in THF at ambient temperature afforded the 1,2-dimethyl-pyrazolin-3-ylidene complexes **2a–c** in 67–94% yield (Scheme 1). The synthesis of complex **2a** by this method has previously been reported [24]. An alternative route to **2a** is reaction of $[(CO)_5Cr{=}C{=}C{=}C(NMe_2)Ph]$ with 1,2-dimethylhydrazine via a substitution/cycloaddition sequence [25]. Another 1,2-dimethyl-pyrazolin-3-ylidene chromium complex (R = H) related to **2a–c** has recently been prepared by thermolysis of the corresponding 1,2-dimethylpyrazolium decacarbonylchromate(-I) [6].

The addition/cyclization reactions (Scheme 1) presumably proceed by initial regioselective Michael addition of



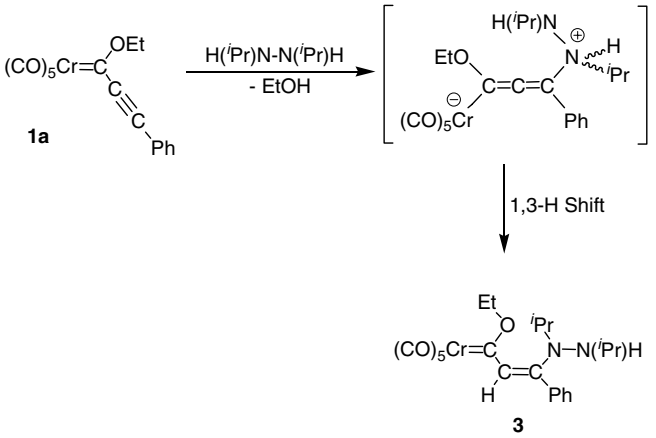
Scheme 1.

one N–H group of the hydrazine to the CC triple bond in **1a–c** and subsequent cyclization and EtOH elimination. The assumption is supported by the results of earlier investigations [23] and by the isolation of an addition product, the corresponding alkenyl(alkoxy)carbene complex **3** (99% yield), when 1,2-dimethylhydrazine was replaced by 1,2-di-*iso*-propylhydrazine in the reaction with **1a** (Scheme 2).

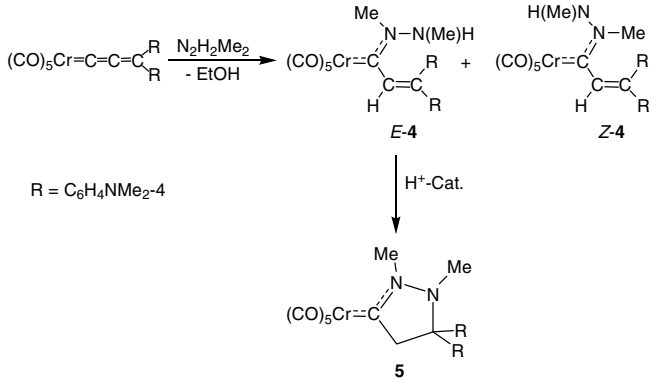
The follow-up cyclization/EtOH elimination was not observed very likely due to steric congestion thus preventing the synthesis of the *N*,*N*-di-*iso*-propyl-substituted pyrazolin-3-ylidene complex by this route.

In neither one of these reactions could the displacement of the ethoxy substituent in **1a–c** by the hydrazine and the formation of an alkynyl(hydrazino)carbene complex be detected. This was also true when the reaction of **1a** with 1,2-di-*iso*-propylhydrazine was carried out at −78 °C. In contrast, the reaction of the tungsten analogue of **1a** with 1,2-dimethylhydrazine at −78 °C afforded 27% of an alkynyl(hydrazino)carbene [23].

For comparison reasons the pyrazolidinylidene complex **5** containing the "saturated" analogue of the pyrazolin-3-ylidene ligand was additionally synthesized (Scheme 3). Addition of 1,2-dimethylhydrazine across the C_α–C_β bond of bis(*p*-dimethylaminophenyl)propadienylidene pentacarbonyl chromium [26] gave an *E*/*Z* mixture of the alke-



Scheme 2.



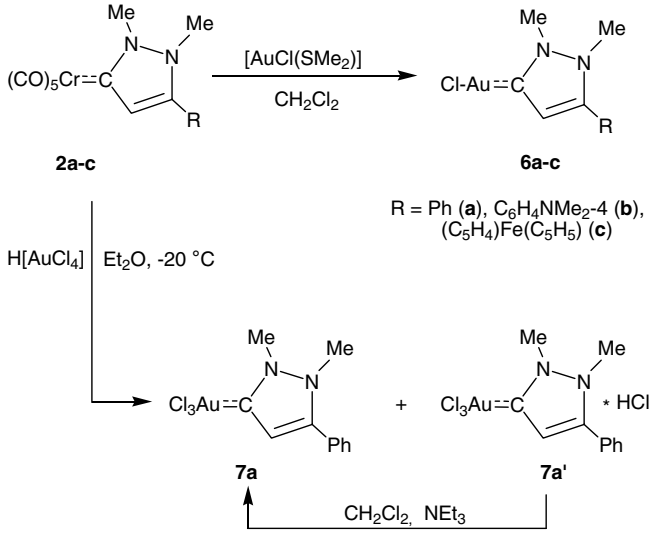
Scheme 3.

nyl(hydrazino)carbene complex **4** [27]. By fractionating crystallization pure *E* isomer could be obtained. Acid-catalyzed ring closure in *E*-**4** finally gave pyrazolidinylidene complex **5**. From the *ν*(CO) spectra it followed that the σ-donor/π-acceptor ratio of the pyrazolidin-3-ylidene ligand in **5** is significantly less than that of the pyrazolin-3-ylidene ligand in **2a**–**c** and is similar to that of the cyclic aminocarbene (1-azacyclopentan-2-ylidene) ligand in $[(CO)_5Cr(\overline{CN(R)CH_2CH_2CH_2})]$ (R = H, alkyl) [28].

2.2. Transfer of the carbene ligand from chromium to gold

The pyrazolin-3-ylidene ligand is readily transferable from chromium to gold(I) and gold(III). When solutions containing equimolar amounts of **2a**–**c** and chloro(dimethylsulfid)gold in dichloromethane were stirred at room temperature, the carbene transfer (Scheme 4) was complete within 30 (**2a**), 120 (**2b**) and 80 (**2c**) minutes, respectively, and the monocarbene complexes **6a**–**c** were isolated in 81% (**6a**), 99% (**6b**) and 71% (**6c**) yield.

When $[AuCl(SMe_2)]$ was replaced by $H[AuCl_4]$ as carbene acceptor, a 1:1 mixture of the monocarbene Au(III) complex **7a** and its hydrochloride **7a′** was obtained (combined yield: 91%) (Scheme 4). On addition of triethylamine the hydrochloride **7a′** was quantitatively transformed into complex **7a**.



Scheme 4.

All complexes were characterized by spectroscopic means and elemental analyses. The structures of **6a**, **6b** and **7a** were additionally established by X-ray structure analyses (Figs. 1–3, Table 1). The five-membered ring is planar, neither atom deviates more than 0.013 Å from the least-squares plane. The intra-ring distances in **6a**, **6b** and **7a** are within error limits identical and are similar to those recently found in related pyrazolin-3-ylidene complexes of chromium [6], palladium [10], rhodium [11] and iron [8]. The aryl ring is strongly twisted against the pyrazolin-3-ylidene ring, the angle between both planes varies between 45.9° (**7a**) and 47.7° (**6b**). As expected Au(III) in **7a** is planar coordinated (sum of angles: 360°), the angle between the *trans*-Cl and the *cis*-Cl ligands being slightly larger than 90°. As with the aryl and the C_3N_2 planes those of the $AuCl_3$ and the C_3N_2 planes are strongly twisted. The angle between both planes is 70.1°. The pronounced donor capacity of the pyrazolin-3-ylidene ligand is evidenced by the *trans* influence of the carbene ligand in **7a**. The

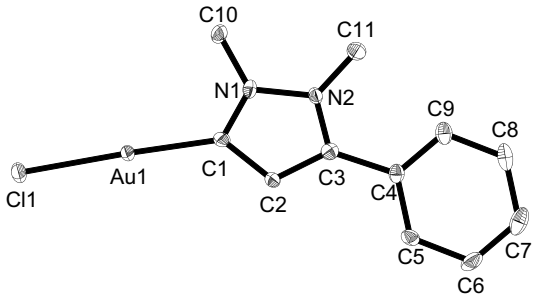


Fig. 1. Structure of complex **6a** in the crystal (ellipsoids drawn at 50% level, hydrogen atoms omitted for clarity). Important angles (°) (for distances see Table 1) are: C(1)–Au(1)–Cl(1) 174.41(19), N(1)–C(1)–C(2) 105.5(5), N(1)–C(1)–Au(1) 124.1(4), C(2)–C(1)–Au(1) 130.1(4), C(1)–N(1)–N(2) 110.6(5), C(3)–N(2)–N(1) 107.9(5), C(3)–C(2)–C(1) 108.3(5), N(2)–C(3)–C(2) 107.8(5).

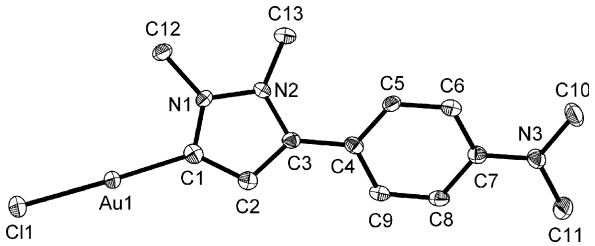


Fig. 2. Structure of complex **6b** in the crystal (ellipsoids drawn at 50% level, hydrogen atoms omitted for clarity). Important angles (°) (for distances see Table 1) are: C(1)–Au(1)–Cl(1) 178.04(16), N(1)–C(1)–C(2) 105.1(4), N(1)–C(1)–Au(1) 120.6(4), C(2)–C(1)–Au(1) 134.3(4), C(1)–N(1)–N(2) 110.9(4), C(3)–N(2)–N(1) 109.1(4), C(1)–C(2)–C(3) 109.5(4), N(2)–C(3)–C(2) 105.4(4).

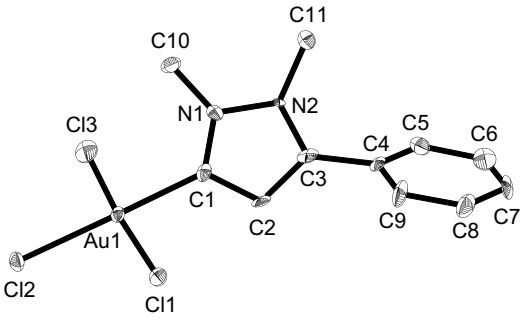


Fig. 3. Structure of complex **7a** in the crystal (ellipsoids drawn at 50% level, hydrogen atoms omitted for clarity). Important distances (Å) and angles (°) (see also Table 1) are: Au(1)–Cl(1) 2.291(2), Au(1)–Cl(2) 2.343(3) ; C(1)–Au(1)–Cl(1) 87.1(3), C(1)–Au(1)–Cl(2) 178.5(3), C(1)–Au(1)–Cl(3) 88.5(3), Cl(1)–Au(1)–Cl(2) 92.43(9), Cl(3)–Au(1)–Cl(2) 92.04(10), Cl(1)–Au(1)–Cl(3) 174.95(10), N(1)–C(1)–C(2) 110.0(9), N(1)–C(1)–Au(1) 123.0(8), C(2)–C(1)–Au(1) 126.8(8), C(1)–N(1)–N(2) 107.4(9), C(3)–N(2)–N(1) 109.1(9), C(3)–C(2)–C(1) 104.8(9), N(2)–C(3)–C(2) 108.6(9).

Au–Cl_{trans} bond (2.343(3) Å) is significantly longer compared to the Au–Cl_{cis} bonds (2.291(2) and 2.288(3) Å).

The reaction of **2a** and **2b** with [AuCl(SMe_2)] was briefly investigated by kinetic means. Both reactions follow a second-order rate law, first order in the concentrations of **2a** (**2b**) and of [AuCl(SMe_2)]. At room temperature, the rate of the reactions is almost independent of the substituent R, the reactions of **2b** being faster by about 10%.

The pyrazolidin-3-ylidene ligand in **5** could likewise be transferred to gold(I) (Scheme 5). However, in contrast to **5** the resulting pyrazolidin-3-ylidene gold(I) complex **8** turned out to be labile and readily decomposed. It was not possible to get pure samples of complex **8** neither by chromatography nor by recrystallization. Therefore, compound **8** was identified only by its ^{1}H NMR and mass spectra.

To determine whether the chloride ligand can be replaced by other more weakly bound anion, a solution of complex **6c** in CH_2Cl_2 was treated with 1.1 equiv. of silver trifluoroacetate. A white precipitate of AgCl quickly formed. The ligand exchange was complete within 20 min at room temperature and complex **9c** (Scheme 6) was isolated as an orange solid in 87% yield. The structure of **9c** was also established by an X-ray structure analysis (Fig. 4, Table 1).

The intra-ring distances are similar to those in **6a** and **6b**. The C_3N_2 ring is tilted against the C_5H_4 ring by 39.7° and 42.3° (two independent molecules) and against the trifluoroacetate plane by 52.3° (49.8°). In the ^{13}C NMR spectrum replacement of the chloro ligand by trifluoroacetate (**6c** → **9c**) gives rise to a significant high-field shift of the Au-bound carbene carbon atom from 168.0 to 158.4 ppm.

2.3. Carbene transfer from chromium to palladium

The pyrazolin-3-ylidene ligand is also transferable to palladium. When solutions of **2a**,**c** in CH_2Cl_2 were stirred at room temperature in the presence of half an equivalent of [$PdCl_2$(NCPh)$_2$] the bis(pyrazolin-3-ylidene) palladium complexes **10a**,**c** were formed quantitatively within about 30–40 min. Complexes **10a** and **10c** were isolated as white or yellow powder in 98% (**10a**) and 90% (**10c**) yield (Scheme 7).

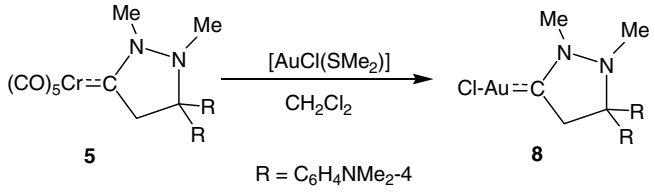
The chloro ligands in **10c** were likewise exchangeable. However, the substitution of iodide for the chloride ligand in **10c** proceeded considerably slower than that of trifluoroacetate for chloride in the gold complex **6c**. When 10 equiv. of sodium iodide were employed the reaction required about 20 h for completion (Scheme 7). Complex **11c** was then obtained in 83% yield.

Analogously to **2a** and **2c**, the pyrazolidin-3-ylidene complex **5** readily reacted with half an equivalent of [$PdCl_2$(NCPh)$_2$] by transmetallation of the heterocyclic carbene ligand (Scheme 8). As already observed with the related pyrazolidin-3-ylidene gold complex **8**, the resulting bis(pyrazolidin-3-ylidene) palladium complex **12** turned

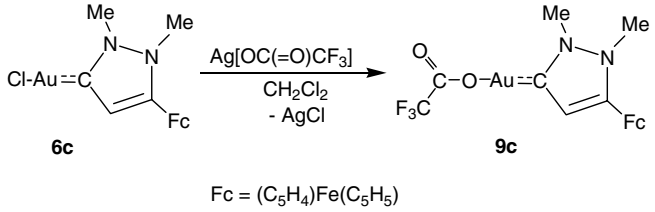
Table 1
Selected distances (Å) and angles (°) in **6a**, **6b**, **7a**, **9c** (all M = Au) and **15a** (M = Pd)

	6a	6b	7a	9c	15a[a]
Distances					
Au–Cl	2.3070(15)	2.2988(13)	2.343(3)[b]	2.055(3)	
M–C1	1.981(6)	1.991(5)	2.015(10)	1.970(4)	1.964/1.965(2)
C1–N1	1.354(8)	1.355(7)	1.342(14)	1.356(5)	1.345/1.349(3)
C1–C2	1.410(7)	1.388(7)	1.398(14)	1.392(5)	1.398/1.396(3)
C2–C3	1.387(8)	1.408(7)	1.386(15)	1.383(5)	1.390/1.396(3)
C3–N2	1.356(8)	1.359(6)	1.357(14)	1.351(5)	1.350/1.351(3)
N1–N2	1.374(7)	1.355(6)	1.362(12)	1.361(5)	1.373/1.364(3)
N1–C10	1.459(7)	1.458(6)	1.442(14)	1.461(5)	1.461/1.459(3)
N2–C11	1.449(8)	1.459(6)	1.464(13)	1.457(5)	1.459/1.459(3)
Angles					
M–C1–N1	124.1(4)	120.6(4)	123.0(8)	122.7(3)	123.3/120.0(2)
M–C1–C2	130.1(4)	134.3(4)	126.8(8)	131.7(3)	130.3/133.7(2)

[a] The second numbers are those of the analogous distances and angle in the second pyrazolin-3-ylidene ligand.
[b] Refers to Au–Cl_{trans}.



Scheme 5.



Scheme 6.

out to be labile and decomposed in part already during the purification procedures (chromatography, recrystallization). Therefore, **12** could not be obtained in a pure form and was identified by its ^{1}H NMR and mass spectrum. Recently, some palladium and rhodium complexes have been prepared and isolated containing 1-azacyclopentan-2-ylidene ligands [29]. The 1-azacyclopentan-2-ylidene ligands in these compounds carry a quarternary carbon atom adjacent the carbene carbon and a bulky 2,6-di-*iso*-propylphenyl group attached to nitrogen. In contrast to **12**, these complexes are stable at room temperature and in air. Their stability presumably arises from the presence of the quarternary carbon atom in the position α to the carbene centre [29].

Tetrahydropyrimidin-4-ylidene palladium complexes were also accessible by the same route. The starting complex **13** has recently been obtained from **2a** by a deprotonation/alkylation sequence [30]. Based on the *ν*(CO) spectra the donor potential of **13** is intermediate between that of **2a** and **5** but somewhat closer to that of **5**. Reaction of **13** with half an equivalent of $[PdCl_2(NCPh)_2]$ afforded complex **14** (Scheme 9) in, after chromatography, 77% yield. In contrast to **12**, complex **14** is stable at room temperature.

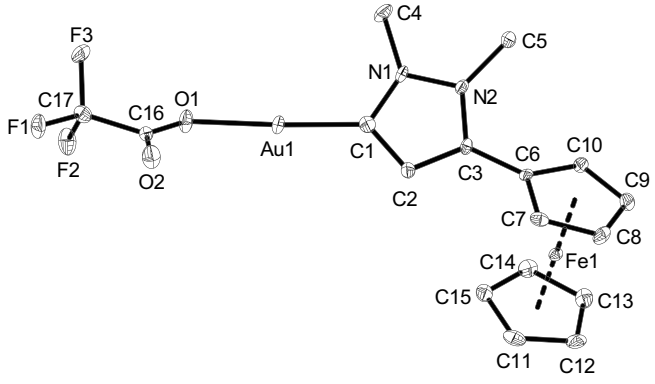
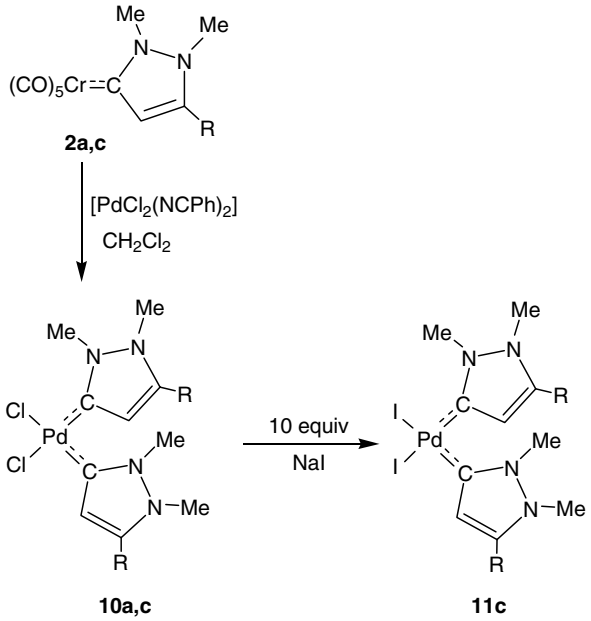
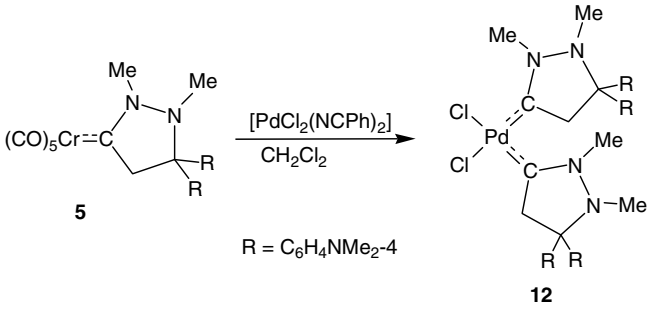


Fig. 4. Structure of complex **9c** in the crystal (ellipsoids drawn at 50% level, hydrogen atoms omitted for clarity). Important distances (Å) and angles (°) (see also Table 1) are: Au(1)–O(1) 2.055(3); C(1)–Au(1)–O(1) 175.65(12), N(1)–C(1)–C(2) 105.5(3), N(1)–C(1)–Au(1) 122.7(3), C(2)–C(1)–Au(1) 131.7(3), C(1)–N(1)–N(2) 110.3(3), C(3)–N(2)–N(1) 108.3(3), C(3)–C(2)–C(1) 108.7(3), N(2)–C(3)–C(2) 107.2(3).

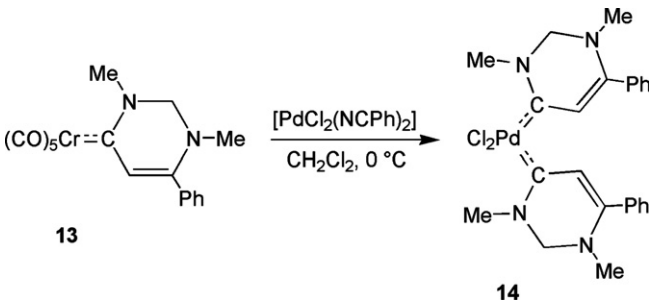


Scheme 7.

The attempt to replace the chloride ligands in **10a** by trifluoroacetate analogously to **6c** → **9c** (Scheme 6) led to an unexpected result. When **10a** was treated with silver trifluoroacetate instead of the expected bis(trifluoroacetato) complex a binuclear Pd–Ag complex was isolated. The new compound (**15a**) contained in addition to two pyrazolin-3-ylidene ligands three trifluoroacetate ligands two of them in a bridging mode (Scheme 10). The solid-state structure of complex **15a** was also established by an X-ray analysis (Fig. 5, Table 1). The palladium atom is square-pyramidal coordinated. The Ag atom occupies the apex position, the two carbene ligands and two oxygen

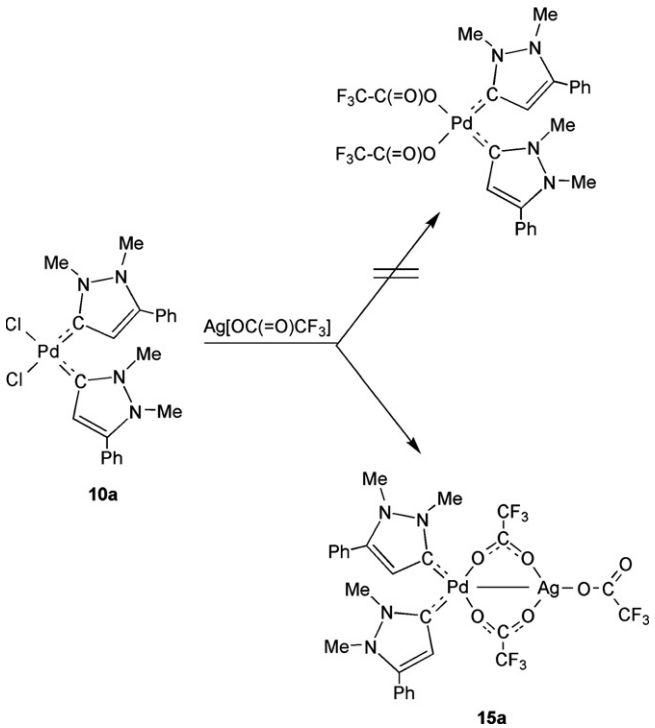


Scheme 8.



Scheme 9.

atoms of the bridging trifluoroacetate ligands assume the four basal positions in a *cis* arrangement. One five-membered ring formed by Pd, Ag and a bridging trifluoroacetate is planar, the other one is slightly twisted (Pd–O–C–O: 1.0° vs. 9.6°). The Pd–Ag bond is very short (2.8752(5) Å) and is even shorter than the Pd–Ag bond in $[PtPdAg(\mu\text{-}PPh_2)_2(C_6F_5)_2(acac)PPh_3]\times 2.5CH_2Cl_2$ (2.886(1) Å) [31], the cation $[PdCl(L)Ag]^{2+}$ (L = 5,8,11-trioxa-2,14-dithia[15]-*m*-cyclophane) (2.884(2) Å) [32], the two-dimensional cationic polymer $[\{Pd_3(S_2CNEt_2)_6Ag_2\}_n]^{2n+}$ (2.933(2) and 3.046(2) Å) [33], the polymer $[[AgPd\{OCHNP(Ph_2)\}\{N(Me_2)CH_2C_6H_4\}]_3]^+$ (2.884(1) Å) [34] and a heterocyclic carbene triflouroacetato $AgPd_2$ complex [35]. Still shorter Ag–Pd distances have only been observed in $[AgPd_2(\mu\text{-}Cl)(\mu\text{-}PPh_2)(\mu\text{-dppe})\{Mn(CO)_4\}_2]$ (2.7259(6) and 2.8014(6) Å) [36]. To prevent steric congestion the carbene planes are tilted by 62.6° and 59.0° against the coordination plane of the Pd atom formed by two bridging O atoms and



Scheme 10.

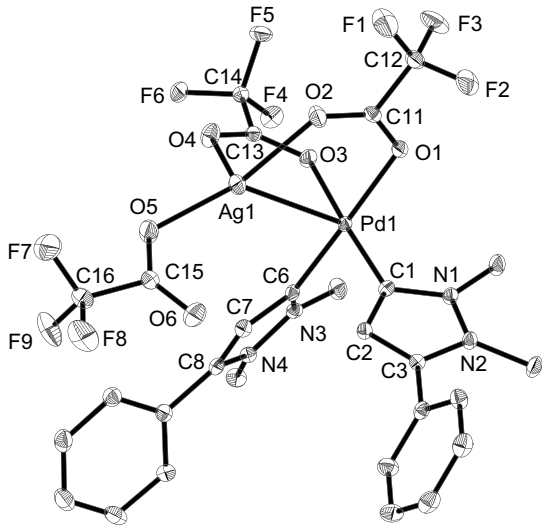


Fig. 5. Structure of complex **15a** in the crystal (ellipsoids drawn at 50% level, hydrogen atoms omitted for clarity). Important distances (Å) and angles (°) (see also Table 1) are: Pd(1)–C(6) 1.964(2), Pd(1)–C(1) 1.965(2), Pd(1)–O(3) 2.0926(18), Pd(1)–O(1) 2.1242(17), Pd(1)–Ag(1) 2.8752(5), Ag(1)–O(5) 2.190(2), Ag(1)–O(2) 2.2794(18), Ag(1)–O(4) 2.4307(19), C(1)–Pd(1)–O(3) 173.29(8), C(6)–Pd(1)–O(1) 178.19(8), C(6)–Pd(1)–Ag(1) 88.69(6), C(1)–Pd(1)–Ag(1) 103.46(6), O(3)–Pd(1)–Ag(1) 83.19(5), O(1)–Pd(1)–Ag(1) 89.57(5), O(5)–Ag(1)–O(2) 146.70(7).

the Pd-bound carbene carbon atoms. The coordination sphere of the Ag atom is a strongly distorted tetrahedron (Pd–Ag–O: 74.66(4), 79.92(4) and 133.85(6)°).

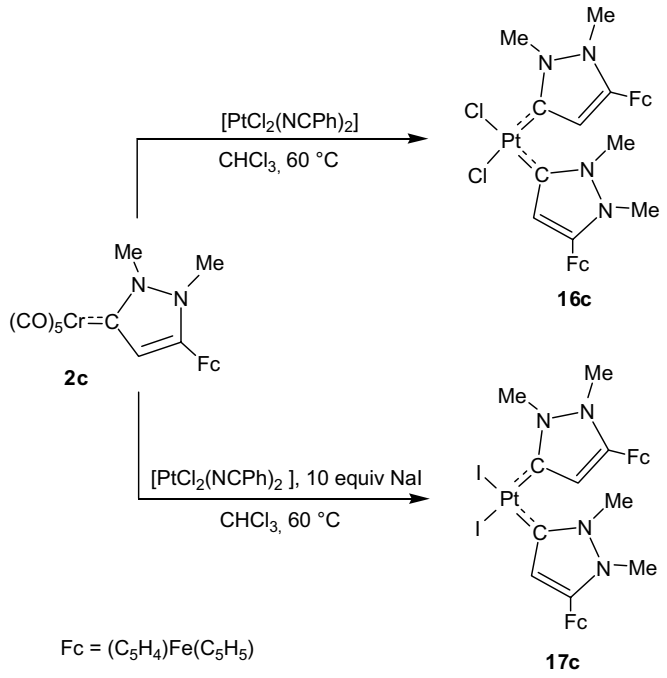
2.4. Carbene transfer from chromium to platinum

The transfer of the heterocyclic carbene ligand in complex **2c** to platinum was achieved by stirring solutions of **2c** and $[PtCl_2(NCPh)_2]$ in boiling $CHCl_3$. The reactions proceeded analogously to those using palladium as the carbene acceptor albeit somewhat slower. When sodium iodide was added to the reaction mixture and the reaction times were extended the bis(iodide)bis(pyrazolin-3-ylidene) platinum complex **17c** was obtained (Scheme 11). Comparison of the spectra of **16c** (**17c**) with those of **10c** (**11c**) indicated that the structures of the platinum complexes are similar to those of the palladium complexes.

2.5. Catalytic applications

The catalytic activities of two mono(pyrazolin-3-ylidene) triphenylphosphane complexes, *cis*-$[PdCl_2(PPh_3)\{\overline{CN(R)N(Me)C(Me)=C(R)}\}]$ (R = Me, Ph), in the Mizoroki–Heck olefination of aryl halides with styrene have recently been investigated. It was found that these complexes show higher yields by a factor of 2 than the analogous imidazol-2-ylidene complexes [10].

We briefly examined the activity of **10a**,**c** in a few C–C coupling reactions. For example both complexes actively catalyzed the reaction of 4-bromoacetophenone with styrene in the presence of 2 mol% of complex **10a** and



Scheme 11.

1.2 equiv. of NaOAc already at 85 °C within 40 h (Table 2). The *isolated* yield of the coupling product *trans*-stilbene was 70%. The ferrocenyl-substituted complex **10c** turned out to be slightly more active than **10a**. When 5 equiv. of $[NBu_4]Br$ was used as the solvent, the catalyst loading could be reduced to 0.5 mol% and the *isolated* yield was 78% at 120 °C (after 15 h) (Table 2). For comparison, both mono(pyrazolin-3-ylidene) complexes gave 98% GC yield at 120 °C in 14 h [10].

The complexes **10a** and **10c** were also active in Suzuki–Miyaura coupling reactions although the activity was only modest (Table 3). Unlike in Mizoroki–Heck reaction, in Suzuki–Miyaura coupling reactions complexes **10a**,**c** were considerably less active than imidazol-2-ylidene complexes [37].

No significant activity was observed in the Stille coupling of phenylethynyl tributyl tin with bromobenzene (solvent: NMP, 3 equiv. of KF, 100 °C, 14 h) neither of **10a** nor of **10c**. Only traces of diphenylacetylene were obtained.

3. Experimental

3.1. General

All operations were performed in an inert gas atmosphere using standard Schlenk techniques. Solvents were dried by distillation from CaH_2 (CH_2Cl_2), $LiAlH_4$ (petrol ether) and sodium (THF, Et_2O). The silica gel used for chromatography (Baker, silica for flash chromatography) was nitrogen saturated. The yields refer to analytically pure compounds and are not optimized. Instrumentation: ^1H NMR and ^{13}C NMR spectra were recorded with a Jeol JNX 400 or a Varian Inova 400 spectrometer at ambient temp. Chemical shifts are relative to the residual solvent or tetramethylsilane peaks. IR: Biorad FTS 60. MS: Finnigan MAT 312. Elemental analysis: Heraeus CHN-O-Rapid. The complexes **1a** [22] and **1c** [23], **2a** [24], *E*-**4** and *Z*-**4** [27], $[(CO)_5Cr{=}C{=}C{=}C(C_6H_4NMe_2\text{-}4)_2]$ [26], **13** [30], $[AuCl(SMe_2)]$ [38,39], $[PdCl_2(NCPh)_2]$ [39] and $[PtCl_2(NCPh)_2]$ [39] and 1,2-di-*iso*-propylhydrazine [40] were prepared according to literature procedures. All other chemicals were commercial products and used as supplied. For the NMR spectra of the cyclic carbene complexes the following numbering scheme has been applied:

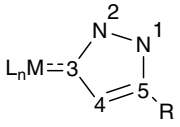
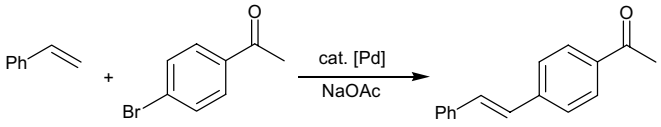


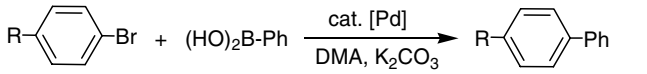
Table 2
Mizoroki–Heck reaction: coupling of 4-bromoacetophenone with styrene catalyzed by complexes **10a** and **10c**[a]



Entry	Cat. [mol%]	Solvent	Temp. (°C)	Time (h)	Yield[b] (%)
1	**10a** [2]	DMA	85	40	70
2	**10a** [1]	NMP	150	14	75
3	**10c** [1]	NMP	150	14	83
4[c]	**10c** [0.5]	$[NBu_4]Br$	120	15	78

[a] Conditions: 1 equiv. of 4-bromacetophenone, 1.5 equiv. of styrene, 1.5 equiv. of sodiumacetate, 3 mL of solvent (DMA, NMP) or 5 equiv. of $[NBu_4]Br$.
[b] Isolated yield.
[c] With 1.2 equiv. of sodium acetate.

Table 3
Suzuki–Miyaura reaction: coupling of aryl bromides with phenylboronic acid catalyzed by **10a** and **10c**[a]



Entry	Cat. [mol%]	R	Temp. (°C)	Time (h)	Yield[b] (%)
1	**10a** [2]	H	100	6	57
2	**10a** [2]	CH_3CO	120	5	5
3	**10c** [1]	H	130	5	50

[a] Conditions: 1 equiv. of aryl bromide, 1.2 equiv. of phenylboronic acid, 1.5 equiv. of potassium carbonate, 2 mL of DMA.
[b] isolated yield.

3.2. Pentacarbonyl[4-dimethylaminophenyl(ethoxy) carbene]chromium (*1b*)

A solution of 6.1 mL of *n*-BuLi (10 mmol, 1.6 M in hexane) was added dropwise at −78 °C to a solution of 1.45 g (10 mmol) 4-dimethylaminophenylacetylene in 20 mL of THF. After 10 min at −78 °C the cooling bath was removed and the solution was stirred for 20 min at 0 °C. Then 2.20 g (10 mmol) of $[Cr(CO)_6]$ was added at 0 °C to the brown solution. The suspension was stirred for approximately 30 min at ambient temp. The progress of the reaction was controlled by IR spectroscopy. When no $[Cr(CO)_6]$ could be detected any more, the solvent was removed in vacuo. The remaining orange-brown residue was dissolved in 20 mL of CH_2Cl_2 and 1.9 g (10 mmol) of $[Et_3O]BF_4$ was added in small portions at 0 °C. The solution was then stirred for about 60 min at ambient temp. The colour of the solution turned dark-violet. The solvent was removed in vacuo. Chromatography of the crude reaction mixture on silica gel at −20 °C using petrol ether/CH_2Cl_2 (ratio decreasing from 8:1 to 5:1) as the eluent an removal of the solvent afforded **1b** as a brown-violet solid. Yield: 3.4 g (8.6 mmol, 86%). Mp 115 °C. IR (CH_2Cl_2, cm^{-1}): ν(CO) = 2051 s, 1941 vs; ν(CC) = 2112 w. ^{1}H NMR (400 MHz, acetone-d_6) $\delta = 7.49$ (d, $J = 8.8$ Hz, 2H, *o*-CH), 6.83 (d, $J = 8.8$ Hz, 2H, *m*-CH), 4.76 (q, $J = 7.2$ Hz, 2H, CH_2), 3.11 (s, 6H, NCH_3), 1.50 (t, $J = 7.2$ Hz, 3H, CH_2CH_3). MS (FAB) *m*/*z* (%): 393 (18) [M^+], 337 (74) [$(M-2CO)^+$], 309 (100) [$(M-3CO)^+$], 253 (90) [$(M-5CO)^+$]. UV–Vis: (λ_{max}/nm ($\log\varepsilon$) [CH_2Cl_2]): 517 (4.454), 397 (4.389). Anal. Calc. for $C_{18}H_{15}CrNO_6$ (393.31): C, 54.97; H, 3.84; N, 3.56. Found: C, 54.45; H, 3.88; N, 3.46%.

3.3. General procedure for the synthesis of 1,2-pyrazolin-3-ylidene chromium complexes

At 0 °C, a solution of 0.40 g (10 mmol) of NaOH in 2 mL of water was added dropwise to a solution of 0.67 g (5 mmol) of 1,2-dimethylhydrazine dihydrochloride in 5 mL of water. The mixture was stirred for 15 min and the resulting solution was added to a deep-purple solution of 4 mmol of the appropriate alkinyl(ethoxy)carbene complex (**1a**–**c**) in 20 mL of THF. Within about one min the solution brightened. The solvent was removed in vacuo. The crude reaction mixture was chromatographed on silica gel at −20 °C using mixtures of petrolether/CH_2Cl_2 as the eluent.

3.4. Pentacarbonyl[5-(4-dimethylaminophenyl)-1, 2-dimethyl-1,2-pyrazolin-3-ylidene]chromium (*2b*)

Yellow-orange solid. Yield: 75%. Mp 195 °C. IR (CH_2Cl_2, cm^{-1}): ν(CO) = 2049 m, 1964 w, 1916 vs. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.25$ (d, $J = 8.6$ Hz, 2H, *o*-CH), 6.76 (d, $J = 8.7$ Hz, 2H, *m*-CH), 6.46 (s, 1H, C^4–H), 4.12 (s, 3H, N^1CH_3), 3.77 (s, 3H, N^2CH_3), 3.04 (s, 6H, $N(CH_3)_2$). ^{13}C NMR (100,5 MHz, $CDCl_3$): $\delta = 223.5$ (*trans*-*C*O), 219.3 (*cis*-*C*O), 192.1 (C^3), 146.5 (C^5), 141.5, 129.7, 120.8, 111.9 (Aryl), 99.3 (C^4), 40.1 ($N(CH_3)_2$), 37.8 (N^1CH_3), 34.9 (N^2CH_3). MS (FAB) *m*/*z* (%): 407 (17) [M^+], 379 (8) [$(M-CO)^+$], 351 (24) [$(M-2CO)^+$], 323 (26) [$(M-3CO)^+$], 295 (100) [$(M-4CO)^+$], 267 (96) [$(M-5CO)^+$]. UV–Vis: (λ_{max}/nm ($\log\varepsilon$) [CH_2Cl_2]): 310 nm (4.376). Anal. Calc. for $C_{18}H_{17}CrN_3O_5$ (407.34): C, 53.07; H, 4.21; N, 10.32. Found: C, 52.56; H, 4.88; N, 9.83%.

3.5. Pentacarbonyl(1,2-dimethyl-5-ferrocenyl-1,2-pyrazolin-3-ylidene)chromium (*2c*)

Orange solid. Yield: 94%. Mp 156 °C (dec). IR (THF, cm^{-1}): ν(CO) = 2048 m, 1960 w, 1917 vs, 1892 m. ^{1}H NMR (400 MHz, acetone-d_6) $\delta = 6.94$ (s, 1H, C^4H), 5.13 (d, $J = 9.8$ Hz, 2H, CH), 4.92 (d, $J = 9.8$ Hz, 2H, CH), 4.70–4.57 (m, 5H, Cp), 3.37 (s, 3H, N^1CH_3), 3.34 (s, 3H, N^2CH_3). ^{13}C NMR (100,5 MHz, acetone-d_6) $\delta = 224.4$ (*trans*-*C*O), 220.5 (*cis*-*C*O), 185.3 (C^3), 144.3 (C^5), 121.8 (C^4) 70.6 (CH), 70.5 (Cp), 69.6 (CH), 38.3 (N^1CH_3), 35.6 (N^2CH_3). MS (FAB) *m*/*z* (%): 472 (25) [M^+], 444 (8) [$(M-CO)^+$], 416 (20) [$(M-2CO)^+$], 388 (23) [$(M-3CO)^+$], 360 (100) [$(M-4CO)^+$], 332 (74) [$(M-5CO)^+$]. UV–Vis: (λ_{max}/nm ($\log\varepsilon$) [CH_2Cl_2]): 262 (4.523). Anal. Calc. for $C_{20}H_{16}N_2O_5CrFe$ (472.20): C, 50.87; H, 3.42; N, 5.93. Found: C, 51.08; H, 3.77; N, 6.04%.

3.6. Pentacarbonyl[3-(N,N′-di-iso-propylhydrazino)-1-ethoxy-3-phenyl-2-propenylidene]-chromium (*3*)

At ambient temp. 0.13 g (1.1 mmol) of 1,2-di-*iso*-propylhydrazine was added to a deep-purple solution of 0.35 g (1 mmol) of **1a** in 5 mL of THF. Within about 1 min the solution brightened and the solvent was removed in vacuo. Chromatography of the crude reaction mixture at −20 °C on silica using petrolether/CH_2Cl_2 (2:1) as the eluent and removal of the solvent in vacuo gave complex **3** as a pale yellow solid. Yield: 99%. Mp 94 °C (dec). IR (THF, cm^{-1}): ν(CO) = 2047 m, 1923 vs, 1905 sh. ^{1}H NMR (400 MHz, acetone-d_6) $\delta = 7.11$ (br, 3H, Aryl-H), 6.89 (br, 2H, Aryl-H), 6.51 (s, 1H, C_βH), 4.62 (s, 1H, NH), 3.87 (br, 2H, OCH_2CH_3), 3.28 (br, 1H, $NCH(CH_3)_2$),

3.21 (br, 1H, NC*H*(CH_3)$_2$), 0.76 (br, 12H, NCH(C*H*$_3$)$_2$), 0.30 (br, 3H, OCH$_2$C*H*$_3$). ^{13}C NMR (100,5 MHz, acetone-d_6) $\delta = 225.1$ (*trans*-CO), 219.7 (*cis*-CO), 214.0 (C_α), 155.8 (C_γ), 138.8, 129.7, 129.5, 128.6 (Aryl), 123.2 (C_β), 73.9 (O*C*H$_2$CH$_3$), 54.6, 46.4 (N*C*H(CH$_3$)$_2$), 21.4, 20.1 (NCH(*C*H$_3$)$_2$), 14.4 (OCH$_2$*C*H$_3$). MS (FAB) *m*/*z* (%): 466 (1) [M^+], 438 (3) [(M−CO)$^+$], 282 (74) [(M−3CO)$^+$], 354 (9) [(M−4CO)$^+$], 326 (100) [(M−5CO)$^+$]. UV–Vis: (λ_{max}/nm (log ε) [solvent]): 435 (4.175) [$CHCl_3$]; 430 (4.229) [CH_2Cl_2]; 423 (4.298) [DMF]. Anal. Calc. for $C_{22}H_{26}N_2O_6Cr$ (466.45): C, 56.65; H, 5.62; N, 6.01. Found: C, 56.92; H, 5.67; N, 5.94%.

3.7. Pentacarbonyl[5,5-bis(4-dimethylaminophenyl)-1,2-dimethyl-pyrazolidin-3-ylidene]-chromium (**5**)

At ambient temp. 260 μL of HBF_4 (0.62 mmol, 54% $HBF_4 \cdot Et_2O$ in Et_2O) were added to a solution of 2.20 g (4.16 mmol) of complex *E*-**4** in 40 mL of CH_2Cl_2. While stirring the mixture for 24 h the colour changed from orange to red. The solvent was removed in vacuo and the crude reaction mixture subjected to chromatography at −20 °C with CH_2Cl_2/Et_2O (1:1) on silica. After removal of the solvent the residue was recrystallized from 90 mL of petrolether/CH_2Cl_2 (9:1). Yellow solid. Yield: 61%. Mp 81–83 °C. IR (THF, cm^{-1}): ν(CO) = 2052 m, 1966 w, 1926 vs, 1911 sh. ^{1}H NMR (400 MHz, CD_2Cl_2) $\delta = 7.10$–6.64 (m, 8H, Aryl-H), 3.96 (br, 2H, CH_2), 3.83 (s, 3H, N^{1}CH$_3$), 2.92 (s, 12H, N(CH$_3$)$_2$), 2.36 (s, 3H, N^{2}CH$_3$). ^{13}C NMR (100.5 MHz, CD_2Cl_2) $\delta = 241.6$ (C^3), 223.6 (*trans*-CO), 218.2 (*cis*-CO), 150.0, 130.6, 128.2, 112.2 (Aryl), 72.8 (C^4), 64.0 (C^5), 41.0 (N^{1}CH$_3$), 40.6 (N(CH$_3$)$_2$), 37.7 (N^{2}CH$_3$). MS (FAB) *m*/*z* (%): 529 (9) [M^+], 501 (4) [(M−CO)$^+$], 473 (7) [(M−2CO)$^+$], 445 (7) [(M−3CO)$^+$], 417 (83) [(M−4CO)$^+$], 389 (100) [(M−5CO)$^+$]. UV–Vis: (λ_{max}/nm (log ε) [CH_2Cl_2]): 266 (4.530). Anal. Calc. for $C_{26}H_{28}N_4O_5Cr$ (528.53): C, 59.09; H, 5.34; N, 10.60. Found: C, 58.40; H, 5.34; N, 10.51%.

3.8. (1,2-Dimethyl-5-phenyl-1,2-pyrazolin-3-ylidene)gold(I) chloride (**6a**)

A solution of 0.29 g (1 mmol) of [AuCl(SMe$_2$)] in 5 mL of CH_2Cl_2 was added at 0 °C to a solution of 0.38 g (1.05 mmol) of **2a** in 5 mL of CH_2Cl_2. The cooling bath was removed and the solution was stirred for 30 min at ambient temp. The colour of the solution gradually changed from yellow to light grey. Then, 30 mL of dry Et_2O was added and the greyish precipitate was filtered off. Repeated recrystallization from CH_2Cl_2/Et_2O gave **5a** as a colourless powder. Yield: 81%. Mp 108 °C (dec). ^{1}H NMR (400 MHz, CD_2Cl_2) $\delta = 7.47$ (br, 3H, Aryl-H), 7.31 (br, 2H, Aryl-H), 6.33 (s, 1H, C^{4}H), 4.11 (s, 3H, N^{1}CH$_3$), 3.76 (s, 3H, N^{2}CH$_3$). ^{13}C NMR (100.5 MHz, CD_2Cl_2) $\delta = 168.5$ (C^3), 148.5 (C^5), 130.8, 129.6, 129.3, 128.1 (Aryl), 116.3 (C^4), 40.1 (N^{1}CH$_3$), 35.2 (N^{2}CH$_3$). MS (FAB) *m*/*z*: 369 [(M−Cl)$^+$]. Anal. Calc. for $C_{11}H_{12}AuClN_2 \times 0.5CH_2Cl_2$ (447.12): C, 30.89; H, 2.93; N, 6.27. Found: C, 31.04; H, 3.05; N, 6.30%.

3.9. (1,2-Dimethyl-5-(4-dimethylaminophenyl)-1,2-pyrazolin-3-ylidene) gold(I) chloride (**6b**)

A solution of 0.147 g (0.5 mmol) of [AuCl(SMe$_2$)] in 15 mL of CH_2Cl_2 was added at 0 °C to a solution of 0.204 g (0.5 mmol) of **2b** in 15 mL of CH_2Cl_2. The colour of the solution rapidly changed to green-black. The reaction mixture was stirred for 2 h at ambient temp. and then fritted. A black solid remained on the frit. The solid was washed three times with 60 mL of Et_2O each. The filtrate was light green. A small portion of charcoal was added and the suspension was filtered over a 2 cm-layer of kieselguhr. The resulting solution was colourless. Removal of the solvent in vacuo gave a white solid. Yield: 0.22 g (99%). Mp 245 °C. ^{1}H NMR (400 MHz, CD_2Cl_2) $\delta = 7.48$ (d, $J = 8.9$ Hz, 2H, *o*-CH), 6.97 (d, $J = 8.8$ Hz, 2H, *m*-CH), 6.43 (s, 1H, C^{4}H), 4.37 (s, 3H, N^{1}CH$_3$), 4.09 (s, 3H, N^{2}CH$_3$), 3.24 (s, 6H, 4-N(CH$_3$)$_2$). ^{13}C NMR (100.5 MHz, CD_2Cl_2) $\delta = 152.0$ (C^3), 149.7 (C^5), 130.2, 115.4, 114.6 (Aryl), 112.3 (C^4), 40.3 (N(CH$_3$)$_2$), 39.3 (N^{1}CH$_3$), 35.2 (N^{2}CH$_3$). MS (FAB) *m*/*z*: 447 (20) [M^+], 412 (100) [(M−Cl)$^+$], 397 (9) [(M−Cl−CH$_3$)$^+$]. UV–Vis: (λ_{max}/nm (log ε) [CH_2Cl_2]): 315 (4.295). Anal. Calc. for $C_{13}H_{17}AuClN_3$ (447.12): C, 34.87; H, 3.83; N, 9.37. Found: C, 34.13; H, 4.01; N, 8.97%.

3.10. (1,2-Dimethyl-5-ferrocenyl-1,2-pyrazolin-3-ylidene)-gold(I) chloride (**6c**)

A solution of 0.33 g (1.12 mmol) of [AuCl(SMe$_2$)] in 5 mL of CH_2Cl_2 was added at ambient temp. to a solution of 0.53 g (1.12 mmol) of **2c** in 5 mL of CH_2Cl_2. The solution was stirred for 80 min at ambient temp. An orange precipitate was formed. Then 70 mL of Et_2O was added and the orange precipitate was filtered off. The solvent was removed in vacuo. Complex **6c** was obtained as an orange solid. Yield: 71%. Mp 188 °C (dec). ^{1}H NMR (400 MHz, CD_2Cl_2) $\delta = 6.19$ (s, 1H, C^{4}H), 4.71 (br, 2H, CH), 4.65 (br, 2H, CH), 4.44 (s, 5H, Cp), 4.34 (s, 3H, N^{1}CH$_3$), 4.20 (s, 3H, N^{2}CH$_3$). ^{13}C NMR (100.5 MHz, $CDCl_3$) $\delta = 168.0$ (C^3), 147.2 (C^5), 116.2 (C^4), 71.6 (C^5*C*), 70.2 (CH) 70.1 (Cp), 69.1 (CH), 39.5 (N^{1}CH$_3$), 34.6 (N^{2}CH$_3$). MS (FAB) *m*/*z* (%): 512 (33) [M^+], 477 (53) [(M−Cl)$^+$], 289 (100) [(M−Cl−Fc−2H)$^+$]. UV–Vis: (λ_{max}/nm (log ε) [CH_2Cl_2]): 441 (2.642). Anal. Calc. for $C_{15}H_{16}AuClFeN_2 \times CH_2Cl_2$ (537.51): C, 32.16; H, 3.04; N, 4.69. Found: C, 32.76; H, 3.18; N, 4.84%.

3.11. (1,2-Dimethyl-5-phenyl-1,2-pyrazolin-3-ylidene)-gold(III) chloride (**7a**) and (1,2-dimethyl-5-phenyl-1,2-pyrazolin-3-ylidene)gold(III) chloride hydrochloride (**7a′**)

A solution of 0.38 g (1.05 mmol) of **2a** in 20 mL of Et_2O was added at −20 °C to a solution of 0.34 g (1 mmol) of

$H[AuCl_4]$ in 30 mL of Et_2O. After 15 min the cooling bath was removed and the solution was stirred for 30 min at ambient temp. A grey solid precipitated. The crude product was filtered off and recrystallized from CH_2Cl_2/Et_2O. Separation of the two products by column chromatography on silica with CH_2Cl_2/acetone (increasing polarity from neat CH_2Cl_2 to CH_2Cl_2/acetone 10:1) gave 0.22 g (0.47 mmol; 47%) of **7a** as a light green powder and 0.23 g (0.44 mmol; 44%) of **7a′** as a yellow powder.

Compound **7a**: Mp 220 °C. ^{1}H NMR (400 MHz, CD_2Cl_2) $\delta = 7.49$–7.39 (m, 5H, Aryl-H), 6.45 (s, 1H, C^4H), 4.17 (s, 3H, N^1CH_3), 3.94 (s, 3H, N^2CH_3). ^{13}C NMR (100.5 MHz, CD_2Cl_2) $\delta = 150.1$ (C^3), 137.5 (C^5), 131.4, 129.6, 129.2, 126.2 (Aryl), 108.1 (C^4), 39.3 (N^1CH_3), 36.1 (N^2CH_3). MS (FAB) *m/z*: 369 [$(M-3Cl)^+$]. Anal. Calc. for $C_{11}H_{12}AuCl_3N_2$ (475.56): C, 27.78; H, 2.54; N, 5.89. Found: C, 27.71; H, 2.69; N, 5.69%.

Compound **7a′**: Mp 151 °C. ^{1}H NMR (400 MHz, CD_2Cl_2) $\delta = 8.12$ (br, 1H, NH), 7.49–7.39 (m, 5H, Aryl), 6.68 (s, 1H, C^4H), 4.21 (s, 3H, NCH_3), 4.00 (s, 3H, NCH_3). ^{13}C NMR (100.5 MHz, CD_2Cl_2) $\delta = 149.3$ (C^3), 140.9 (C^5), 130.6, 129.6, 129.2, 125.8, (Aryl), 112.2 (C^4), 39.4 (N^1CH_3), 35.8 (N^2CH_3). MS (FAB) *m/z*: 369 [$(M-3Cl)^+$]. Anal. Calc. for $C_{11}H_{12}AuCl_3N_2 \times HCl$ (512.02): C, 25.80; H, 2.56; N, 5.47. Found: C, 25.85; H, 2.71; N, 5.45%.

3.12. Transformation of 7a′ into 7a

At ambient temp. 0.5 mL of Et_3N were added to a solution of 0.10 g (0.2 mmol) of **7a′** in 2 mL of CH_2Cl_2. After 5 min the crude reaction mixture was filtered over a short plug of silica using CH_2Cl_2 as eluent. Evaporation of the solvent gave 95 mg (0.2 mmol; 100%) of pure **7a**.

3.13. [1,2-Dimethyl-5,5-bis-(p-dimethylaminophenyl)-pyrazolidin-3-ylidene]gold(I) chloride (8)

The synthesis of complex **8** from **5** and $[AuCl(SMe_2)]$ was carried out analogously to that of **6a**. Complex **8** was labile and readily decomposed, partly even on chromatography at low temp. Therefore, **8** could not be obtained in a pure form. It was identified by its ^{1}H NMR and mass spectra. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 6.87$ (d, $J = 8.6$ Hz, 4H, *o*-CH), 6.57 (d, $J = 8.6$ Hz, 4H, *m*-CH), 3.66 (s, 3H, N^1CH_3), 3.53 (s, 2H, CH_2), 2.88 (s, 12H, $N(CH_3)_2$), 2.34 (s, 3H, N^2CH_3). MS (FAB) *m/z* (%): 568 (16) [M^+], 533 (11) [$(M-Cl)^+$].

3.14. (1,2-Dimethyl-5-ferrocenyl-1,2-pyrazolin-3-ylidene)gold(I) trifluoroacetate (9c)

Silvertrifluoroacetate (0.11 g, 0.51 mmol) was added to a solution of 0.24 g (0.47 mmol) of **6c** in 20 mL of dry CH_2Cl_2. The solution was stirred for 20 min at ambient temp. A white precipitate of AgCl formed which was filtered off. The filtrate was concentrated and the product **9c** was obtained as an orange solid. Yield: 87%. Mp 118 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 6.47$ (s, 1H, C^4H), 4.53 (br, 2H, CH), 4.50 (br, 2H, CH), 4.24 (s, 5H, Cp), 4.16 (s, 3H, N^1CH_3), 3.95 (s, 3H, N^2CH_3). ^{13}C NMR (100.5 MHz, $CDCl_3$) $\delta = 158.4$ (C^3), 147.6 (C^5), 116.7 (C^4), 71.3 (C^5C), 70.4 (CH), 70.2 (Cp), 69.1 (CH), 39.6 (N^1CH_3), 34.6 (N^2CH_3), not observed (CF_3COO). MS (FAB) *m/z* (%): 521 (4) [$(M-CF_3)^+$], 477 (100) [$(M-COOCF_3)^+$], 357 (21) [$(M-COOCF_3-Cp-Fe)^+$]. UV–Vis: (λ_{max}/nm ($\log\varepsilon$) [CH_2Cl_2]): 489 (2.399). Anal. Calc. for $C_{17}H_{16}AuF_3FeN_2O_2$ (590.13): C, 34.60; H, 2.73; N, 4.75. Found: C, 35.40; H, 3.18; N, 4.79%.

3.15. cis-Bis(1,2-dimethyl-5-phenyl-1,2-pyrazolin-3-ylidene)palladium(II) chloride (10a)

A solution of 0.19 g (0.5 mmol) of $[PdCl_2(NCPh)_2]$ in 10 mL of CH_2Cl_2 was added at 0 °C to a solution of 0.38 g (1.05 mmol) of **2a** in 5 mL of CH_2Cl_2. The cooling bath was removed and the solution was stirred for 30 min at ambient temp. The colour of the reaction mixture gradually changed from yellow to black. Then, 40 mL of Et_2O was added and the greyish precipitate was filtered off. Repeated recrystallization from CH_2Cl_2/pentane gave **10a** as a white powder. Yield: 98%. Mp 192 °C. ^{1}H NMR (400 MHz, CD_2Cl_2) $\delta = 7.43$–7.31 (m, 10H, Aryl), 6.30 (s, 2H, C^4H), 4.42 (s, 6H, N^1CH_3), 3.68 (s, 6H, N^2CH_3). ^{13}C NMR (100.5 MHz, CD_2Cl_2) $\delta = 180.4$ (C^3), 147.3 (C^5), 130.6, 129.5, 129.2, 128.4 (Aryl), 114.7 (C^4), 39.7 (N^1CH_3), 34.9 (N^2CH_3). MS (FAB) *m/z*: 487 [$(M-Cl)^+$]. Anal. Calc. for $C_{22}H_{24}Cl_2N_4Pd \times 0.25CH_2Cl_2$ (543.02): C, 49.21; H, 4.55; N, 10.32. Found: C, 49.24; H, 4.85; N, 10.37%.

3.16. cis-Bis(1,2-dimethyl-5-ferrocenyl-1,2-pyrazolin-3-ylidene)palladium(II) chloride (10c)

A solution of 0.19 g (0.5 mmol) of $[PdCl_2(NCPh)_2]$ in 6 mL of CH_2Cl_2 was added at ambient temp. to a solution of 0.47 g (1.0 mmol) of **2c** in 6 mL of CH_2Cl_2. The solution was stirred for 40 min. The colour of the reaction mixture gradually changed from yellow to black. The volume of the solution was reduced in vacuo to about 6 mL. When 15 mL of Et_2O was added, a greyish precipitate formed that was filtered off. Repeated recrystallization from CH_2Cl_2/pentane yielded **10c** as a yellow powder. Yield: 90%. Mp 193 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 6.33$ (br, 2H, C^4H), 4.46–4.36 (m, 8H, CH), 4.31 (br, 6H, N^1CH_3), 4.09 (s, 5H, Cp), 4.08 (s, 5H, Cp), 3.80 (br, 6H, N^2CH_3). ^{13}C NMR (100.5 MHz, CD_2Cl_2) $\delta = 176.3$ (C^3), 145.5 (C^5), 114.5 (C^4), 71.7 (C^5C), 70.1 (CH), 70.0 (Cp), 68.9 (CH), 41.1 (N^1CH_3), 33.9 (N^2CH_3). MS (FAB) *m/z* (%): 737 (3) [M^+], 702 (44) [$(M-Cl)^+$], 665 (22) [$(M-2Cl)^+$], 384 (15) [$(M-2Cl-NHC)^+$], 281 (100) [$(M-2Cl-NHC-Pd)^+$]. UV–Vis: (λ_{max}/nm ($\log\varepsilon$) [CH_2Cl_2]): 448 (2.843). Anal. Calc. for $C_{30}H_{32}Cl_2Fe_2N_4Pd \times CH_2Cl_2$ (822.56): C, 45.27; H, 4.17; N, 6.81. Found: C, 44.60; H, 4.62; N, 6.80%.

3.17. cis-Bis(1,2-dimethyl-5-ferrocenyl-1,2-pyrazolin-3-ylidene)palladium(II) iodide (**11c**)

A solution of 0.11 g (0.29 mmol) of $[PdCl_2(NCPh)_2]$ and 0.27 g (0.57 mmol) of **2c** in 5 mL of CH_2Cl_2 was charged with 0.44 g (2.9 mmol) of NaI. The mixture was stirred for 20 h at ambient temp. When all of the reactants had been consumed (controlled by IR spectroscopy) activated carbon was added to the black reaction mixture. Filtration over kieselguhr gave an orange solution. The solvent was removed in vacuo and the residue was repeatedly recrystallized from CH_2Cl_2/pentane affording **11c** as an orange powder. Yield: 83%. Mp 117 °C (dec). ^{1}H NMR (400 MHz, 1,1,2,2-tetrachlorethane-d_2) $\delta = 6.19$ (br, 2H, C^4H), 4.59 (br, 4H, CH), 4.51 (br, 4H, CH), 4.39 (s, 5H, Cp), 4.37 (s, 5H, Cp), 4.17 (br, 6H, N^1CH_3), 4.13 (br, 6H, N^2CH_3). ^{13}C NMR (100.5 MHz, 1,1,2,2-tetrachlorethane-d_2) $\delta = 173.9$ (C^3), 145.1 (C^5), 114.1 (C^4), 72.1 (C^5C), 70.1 (Cp), 70.0 (*C*H), 68.9 (CH), 40.2 (N^1CH_3), 34.4 (N^2CH_3). MS (FAB) *m*/*z* (%): 794 (10) [$(M-I)^+$], 666 (6) [$(M-2I)^+$], 545 (9) [$(M-2I-Cp-Fe)^+$], 424 (20) [$(M-2I-2Cp-2Fe)^+$]. UV–Vis: (λ_{max}/nm ($\log\varepsilon$) [CH_2Cl_2]): 441 (2.926). Anal. Calc. for $C_{30}H_{32}I_2Fe_2N_4Pd \times CH_2Cl_2$ (1005.45): C, 37.03; H, 3.41; N, 5.57. Found: C, 37.38; H, 3.37; N, 4.92%.

3.18. cis-Bis(5,5-bis(p-dimethylaminophenyl)-1,2-dimethyl-pyrazolidin-3-ylidene)palladium(II) chloride (**12**)

The synthesis of complex **12** from **5** and $[PdCl_2(NCPh)_2]$ was carried out analogously to that of **10a**. Complex **12** was labile and readily decomposed partly even on chromatography at low temp. Therefore, **12** could not be obtained in a pure form. It was identified by its ^{1}H NMR and mass spectra. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 6.95$ (d, $J = 7.0$ Hz, 8H, *o*-CH), 6.55 (d, $J = 7.8$ Hz, 8H, *m*-CH), 3.08 (br, 4H, CH_2), 2.96 (br, 6H, N^1CH_3), 2.87 (br, 24H, $N(CH_3)_2$), 2.83 (br, 6H, N^2CH_3). MS (FAB) *m*/*z* (%): 850 (4) [M^+], 815 (17) [$(M-Cl)^+$].

3.19. cis-Bis(1,3-dimethyl-6-phenyl-dihydro-pyrimidin-4-ylidene)palladium(II) chloride (**14**)

A solution of 46 mg (0.12 mmol) of $[PdCl_2(NCPh)_2]$ in 5 mL of CH_2Cl_2 was added at 0 °C to a solution of 90 mg (0.24 mmol) of **13** in 2 mL of CH_2Cl_2. The cooling bath was removed and the solution was stirred for 30 min at ambient temp. The colour of the reaction mixture gradually changed from yellow to brown. Then, 40 mL of Et_2O was added and the greyish precipitate was filtered off. Repeated recrystallization from CH_2Cl_2/pentane afforded **14** as a yellow powder. Yield: 77%. ^{1}H NMR (400 MHz, CD_2Cl_2) $\delta = 7.55$–7.43 (m, 10H, Aryl), 6.38 (s, 2H, C^5H), 4.56 (br, 4H, NCH_2N), 4.04 (s, 6H, N^1CH_3), 2.88 (s, 6H, N^2CH_3). ^{13}C NMR (100.5 MHz, CD_2Cl_2) $\delta = 162.2$ (C^4), 151.3 (C^6), 132.8, 131.4, 129.9, 129.2 (Aryl), 111.6 (C^5), 68.2 (NCH_2N), 41.2 (N^1CH_3), 39.1 (N^2CH_3). MS (FAB) *m*/*z*: 515 [$(M-Cl)^+$]. Anal. Calc. for $C_{24}H_{28}Cl_2N_4Pd \times 0.5CH_2Cl_2$ (634.77): C, 49.68; H, 4.93; N, 9.46. Found: C, 49.91; H, 5.17; N, 9.66%.

3.20. cis-Bis(1,2-dimethyl-5-phenyl-1,2-pyrazolin-3-ylidene)-palladium(II)-bis(μ-trifluoro-acetato)silver(I) trifluoroacetate (**15a**)

A solution of 0.31 g (0.59 mmol) of **10a** in 10 mL of CH_2Cl_2 was added at ambient temp. to a solution of 0.26 g (1.18 mmol) of silver trifluoroacetate in 5 mL of CH_2Cl_2. The solution was stirred for 20 min at ambient temp. A white precipitate of AgCl formed and was filtered off. The filtrate was concentrated and the product **15a** was obtained as an off-white powder. Yield: 60%. Mp 118 °C (dec). ^{1}H NMR (400 MHz, CD_2Cl_2) $\delta = 7.25$–7.41 (m, 10H, Aryl), 6.74 (s, 2H, C^4H), 4.20 (s, 6H, N^1CH_3), 3.68 (s, 6H, N^2CH_3). ^{13}C NMR (100.5 MHz, CD_2Cl_2) $\delta = 154.3$ (C^3), 148.0 (C^5), 127.6, 129.2, 129.4, 130.8 (Aryl), 115.9 (C^4), 39.2 (N^1CH_3), 35.1 (N^2CH_3), CF_3COO not observed. MS (FAB) *m*/*z*: 563 (56) [$(M-Ag-2CF_3COO)^+$], 450 (16) [$(M-Ag-3CF_3COO)^+$]. UV–Vis: (λ_{max}/nm ($\log\varepsilon$) [CH_2Cl_2]): 255 (4.543). Anal. Calc. for $C_{28}H_{24}AgF_9N_4O_6Pd$ (897.80): C, 37.46; H, 2.69; N, 6.24. Found: C, 38.28; H, 3.18; N, 6.24%.

3.21. cis-Bis(1,2-dimethyl-5-ferrocenyl-1,2-pyrazolin-3-ylidene)platinum(II) chloride (**16c**)

A solution of 0.20 g (0.42 mmol) of $[PtCl_2(NCPh)_2]$ in 5 mL of $CHCl_3$ was added at ambient temp. to a solution of 0.40 g (0.85 mmol) of **2c** in 5 mL of $CHCl_3$. The solution was stirred for 2 h at 60 °C. The colour of the reaction mixture gradually changed from orange to black. When 15 mL of Et_2O was added an orange precipitate formed that was filtered off. Repeated recrystallization from CH_2Cl_2/pentane gave **16c** as a yellow powder. Yield: 79%. Mp 159 °C (dec). ^{1}H NMR (400 MHz, CD_2Cl_2) $\delta = 6.26$ (br, 2H, C^4H), 4.44 (br, 6H, N^1CH_3), 4.33 (br, 8H, CH), 4.16 (br, 6H, N^2CH_3), 4.09 (br, 10H, Cp). ^{13}C NMR (100.5 MHz, CD_2Cl_2) $\delta = 149.6$ (C^3), 138.9 (C^5), 115.6 (C^4), 72.7 (C^5C), 71.5–69.6 (Cp, CH), 29.7 (N^1CH_3), 25.3 (N^2CH_3). MS (FAB) *m*/*z*: 825 (37) [M^+], 790 (100) [$(M-Cl)^+$], 755 (21) [$(M-2Cl)^+$]. UV–Vis: (λ_{max}/nm ($\log\varepsilon$) [CH_2Cl_2]): 449 (2.902). Anal. Calc. for $C_{30}H_{32}Cl_2Fe_2N_4Pt \times 0.5CHCl_3$ (885.28): C, 41.35; H, 3.70; N, 6.32. Found: C, 41.54; H, 4.13; N, 6.25%.

3.22. cis-Bis(1,2-dimethyl-5-ferrocenyl-1,2-pyrazolin-3-ylidene)platinum(II) iodide (**17c**)

NaI (1.35 g, 9.0 mmol) was added to a solution of 0.21 g (0.45 mmol) of $[PtCl_2(NCPh)_2]$ and 0.42 g (0.90 mmol) of **2c** in 10 mL of $CHCl_3$. The solution was stirred for 3 h at 60 °C and 15 h at ambient temp. The colour of the reaction mixture gradually changed from orange to black. Then

15 mL of Et_2O was added and the orange precipitate was filtered off. Repeated recrystallization from CH_2Cl_2/pentane gave **17c** as a golden-coloured solid. Yield: 87%. Mp 140 °C (dec). ^1H NMR (400 MHz, CD_2Cl_2) $\delta = 6.67$ (s, 2H, C^4H), 4.67 (br, 4H, CH), 4.52 (br, 4H, CH), 4.43 (br, 6H, N^1CH_3), 4.29 (br, 6H, N^2CH_3), 4.26 (br, 10H, Cp). ^{13}C NMR (100.5 MHz, CD_2Cl_2) $\delta = 150.9$ (C^3), 137.4 (C^5), 107.5 (C^4), 71.7 (C^5C), 70.9 (Cp), 70.6 (CH), 69.9 (CH), 39.4 (N^1CH_3), 36.5 (N^2CH_3). MS (FAB) *m/z*: 883 (4) [$(M-I)^+$], 755 (1) [$(M-2I)^+$], 289 (100) [$(M-2I-NHC-Fc)^+$], 280 (95) [$(M-2I-NHC-Pt)^+$]. UV–Vis: (λ_{max}/nm ($\log\varepsilon$) [CH_2Cl_2]): 359 (3.939). Anal. Calc. for $C_{30}H_{32}Fe_2I_2N_4Pt \times 1.5CHCl_3$ (1188.25): C, 31.84; H, 2.84; N, 4.72. Found: C, 31.02; H, 3.27; N, 4.70%.

3.23. Representative example for the Heck reaction of bromoacetophenone with styrene catalyzed by 1,2-pyrazolin-3-ylidene complexes

A suspension of 7.4 mg (1 mol%) of **10c**, 123 mg (1.5 mmol) of sodium acetate, 199 mg (1.0 mmol) of 4-bromoacetophenone and 0.17 mL (1.5 mmol) of styrene in 3 mL of *N*-methyl-2-pyrrolidinone (NMP) was degassed twice at ambient temp. and then stirred at 150 °C until complete conversion of the arylhalide was indicated by TLC (ca. 14 h). The reaction mixture was diluted with 20 mL of H_2O and extracted three times with 20 mL of Et_2O each. The combined organic layers were dried over anhydrous $MgSO_4$ and filtered. The solvent was evaporated in vacuo and the residue was chromatographed on silica (eluent: pentane/CH_2Cl_2 2:1) yielding 184 mg (83%) of *trans*-stilbene. The stilbene was identified by comparison of its spectra with those of an authentic sample.

3.24. Representative example for the Suzuki reaction of aryl bromides with phenylboronic acid catalyzed by 1,2-pyrazolin-3-ylidene complexes

A suspension of 10.0 mg (2 mol%) of **10a**, 200 mg (1.5 mmol) of potassium carbonate, 0.11 mL (1.0 mmol) of bromobenzene and 148 mg (1.2 mmol) of phenylboronic acid in 2 mL of DMA was degassed twice at ambient temp. and then stirred at 100 °C until complete conversion of the arylhalide was indicated by TLC (ca. 6 h). The reaction mixture was diluted with 20 mL of H_2O and extracted three times with 20 mL of Et_2O each. The combined organic layers were dried over anhydrous $MgSO_4$ and filtered. The solvent was evaporated in vacuo and the residue was chromatographed on silica (eluent: pentane) yielding 88 mg (57%) of biphenyl as colourless crystals. Biphenyl was identified by comparison of its spectra with those of an authentic sample.

3.25. X-ray structure analysis of *6a, 6b, 7a, 9c and 15a*

Single crystals of **6a** · ($0.5CH_2Cl_2$), **6b**, **7a**, **9c** and **15a** · ($2CH_2Cl_2$) suitable for X-ray structure analyses were obtained by slow diffusion of *n*-hexane into solutions of **6a**, **6b**, **7a**, **9c** and **15a** in CH_2Cl_2 at 4 °C. The measurements were performed with a crystal mounted on a glass fibre on a Siemens P4 diffractometer (**6a**) or on a Stoe IPDS II diffractometer (all others, each: graphite monochromator, Mo Kα, radiation, $\lambda = 0.71073$ Å). The structures were solved by Patterson methods (**6a** and **7a**) and by direct methods (**6b**, **9c** and **15a**), respectively, using the SHELXTL-97 program package [41]. The position of the hydrogen atoms were calculated by assuming ideal geometry and

Table 4
Crystallographic data and refinement details for the complexes **6a** × $0.5CH_2Cl_2$, **6b**, **7a**, **9c** and **15a** × $2CH_2Cl_2$

	6a	**6b**	**7a**	**9c**	**15a**
Formula	$C_{11.5}H_{13}AuCl_2N_2$	$C_{13}H_{17}AuClN_3$	$C_{11}H_{12}AuCl_3N_2$	$C_{17}H_{16}AuF_3FeN_2O_2$	$C_{30}H_{28}AgCl_4F_9N_4O_6Pd$
M_r	447.11	447.71	475.54	590.13	1067.63
Crystal size (mm)	0.40 × 0.30 × 0.20	0.20 × 0.16 × 0.10	0.50 × 0.37 × 0.20	0.40 × 0.30 × 0.20	0.40 × 0.30 × 0.20
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Triklin	Monoclinic
Space group	*P*2(1)2(1)2(1)	*P*21/*c*	*P*21/*c*	$P\bar{1}$	*P*2(1)/n
a (Å)	17.070(3)	7.3231(15)	9.2963(19)	7.3116(15)	12.334(3)
b (Å)	7.4910(15)	6.7798(14)	14.170(3)	15.128(3)	14.233(3)
c (Å)	10.537(2)	28.573(6)	10.622(2)	16.155(3)	22.003(4)
α (°)	90	90	90	100.78(3)	90
β (°)	90	92.26(3)	100.81(3)	97.63(3)	91.17(3)
γ (°)	90	90	90	101.44(3)	90
V (Å^3)	1347.4(5)	1417.5(5)	1374.4(5)	1693.5(6)	3861.8(13)
Z	4	4	4	4	4
μ (mm^{-1})	11.292	10.553	11.265	9.555	1.339
θ Range (°)	3.54–29.15	2.78–25.15	3.64–29.06	3.43–25.69	3.41–29.28
Index ranges (*h*,*k*,*l*)	±23, ±10, ±14	±8, ±8, −33/34	±12, 0/19, 0/14	±8, ±18, ±19	±16, ±19, ±30
Reflections collected	23989	16641	3514	22623	69254
Independent reflections/R_{int}	3634/0.1347	2507/0.0683	3514/0.0000	6348/0.0371	10400/0.1140
Observed reflections ($I > 2\sigma(I)$)	3555	2355	2736	5261	8541
Parameters	150	163	154	469	496
R_1/wR_2 ($I > 2\sigma(I)$)	0.0305/0.0746	0.0241/0.0558	0.054/0.1435	0.0217/0.0373	0.0336/0.0711
R_1/wR_2 (all data)	0.0315/0.0750	0.0271/0.0569	0.0738/0.1567	0.0317/0.0391	0.0474/0.0749
Goodness-of-fit on F^2	1.049	1.145	1.046	1.039	1.018

their coordinates were refined together with those of the attached carbon atoms as riding-model. All other atoms were refined anisotropically. For the crystallographic data and the refinement details see Table 4.

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Appendix A. Supplementary material

CCDC 637547, 637548, 637549, 637550 and 637551 contain the supplementary crystallographic data for **6a** · ($0.5CH_2Cl_2$), **6b**, **7a**, **9c** and **15a** · ($2CH_2Cl_2$). These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.03.022.

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