CHEMISTRY A European Journal



Accepted Article

Title: Metal Complexes of a Redox-Active [1]Phosphaferrocenophane: Structures, Electrochemistry and Redox-Switchable Catalysis

Authors: Alexander Feyrer, Markus Armbruster, Karin Fink, and Frank Breher

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Chem. Eur. J. 10.1002/chem.201700868

Link to VoR: http://dx.doi.org/10.1002/chem.201700868

Supported by ACES



COMMUNICATION

Metal Complexes of a Redox-Active [1]Phosphaferrocenophane: Structures, Electrochemistry and Redox-Induced Catalysis

Alexander Feyrer,^[a] Markus K. Armbruster,^[b] Karin Fink,^[b] and Frank Breher*^[a]

Dedicated to Prof. Dieter Fenske on occasion of his 75th birthday.

Abstract: The synthesis and characterisation of several metal complexes of a redox-active, mesityl(Mes)-substituted [1]phosphaferrocenophane, FcPMes (1), are reported. Cyclic voltammetry studies on the bimetallic complexes [M($\kappa^1 P$ -1)(cod)Cl] (M = Rh: 2; M = Ir: 4), $[Rh(\kappa^1 P-1)_2(CO)CI]$ (3) and $[AuCl(\kappa^1 P-1)]$ (5), in conjunction with DFT calculations, provided indications for a good electronic communication between the metal atoms. In order to confirm that the ferrocenophane unit might be able to electrochemically influence the reactivity of the coordinated transition metal, the rhodium complex 2 was employed as stimuli-responsive catalyst in the hydrosilylation of terminal alkynes. All reactions were greatly accelerated with in situ generated 2⁺ as a catalyst as compared to 2. Even more importantly, a markedly different selectivity was observed. Both factors were attributed to different mechanisms operating for 2 and 2⁺ (alternative Chalk-Harrod and Chalk-Harrod mechanism, respectively). DFT calculations revealed relatively large differences for the activation barriers for 2 and 2⁺ in the reductive elimination step of the classical Chalk-Harrod mechanism. Thus, the key to the understanding is a cooperative "oxidatively induced reductive elimination" step, which facilitates both a higher activity and a markedly different selectivity.

Stimuli-responsive homogeneous catalysts whose activity and/or selectivity can be modulated by an external, non-invasive stimulus have been the subject of many current research activities.^[1] Most efforts so far have been devoted to on-off switching of catalytic activity. Selected examples containing a redox-active metalloligand, which were employed in redox-switchable/redox-induced catalysis, are depicted in Scheme 1. Pioneering work in this area have been performed by Wrigthon and co-workers by employing the oxidised and reduced form of I in rhodium-catalysed hydrogenation and hydrosilylation reactions.^[2] In following years, the redox-controlled polymerisation has received much attention by various groups (e.g., II – IV, VIII).^[3,4] More recently, some gold complexes featuring redox-responsive carbene ligands (V, VI) have been success-

[a] Dr. A. Feyrer, Prof. Dr. F. Breher Institute of Inorganic Chemistry Division Molecular Chemistry Karlsruhe Institute of Technology (KIT) Engesserstr. 15 76131 Karlsruhe, Germany E-mail: breher@kit.edu
[b] Dr. M. K. Armbruster, PD Dr. K. Fink Institute of Nanotechnology Karlsruhe Institute of Technology (KIT) Postfach 3630 76021 Karlsruhe, Germany)

Supporting information for this article is given via a link at the end of the document.

fully applied in redox-induced gold catalysis.^[5] Our group has reported on bimetallic complexes of the closely related, redoxactive C-^[6] and Ge-based^[7] metalloligands (VII, IX). The electronic metal-to-metal communication, e.g. for IX, was found to be efficient due to the close proximity of the metal atoms. Applications in stimuli-responsive catalysis have, however, been hampered so far due to the high moisture sensitivity of the complexes. We have therefore turned our focus to phosphinebased metalloligands while retaining the arrangement of the metal atoms in the same region of space. Even though [1]phosphaferrocenophanes^[8] were studied in great detail in the past, mainly for the synthesis of metallopolymers, investigations of their transition metal complexes - especially the role of the ferrocenophane unit^[9] as a redox-active ligand - are rare. In view of our interest to explore cooperative effects in multimetallic complexes^[10] we present herein our studies on their applicability in redox-switchable/redox-induced catalysis.



Scheme 1. Selected redox-switchable bimetallic complexes from the literature. Most of them have been applied in redox-switchable/redox-induced catalysis.

The metalloligand $1^{[8g]}$ (Scheme 2) was prepared according to published procedures from dilithiated ferrocene TMEDA adduct and MesPCl₂ and obtained as dark-red needles after work-up. The complexes **2**, **4** and **5** were prepared by adding **1** to a solution of the respective metal precursor at low temperatures and obtained in good yields as orange to red needles (**2** and **4**) or as dark-red crystals (**5**) after crystallisation (Scheme 2). Reaction of **2** with CO in dichloromethane or toluene led to complex **3** instead of the expected bis(carbonyl) complex (**3**')

COMMUNICATION

and was obtained as an orange solid after work-up (see also footnote [11]). All complexes are slightly air-sensitive with **5** being additionally sensitive to light. Upon coordination to a transition metal fragment, the ³¹P NMR chemical shifts are detected at higher frequencies ($\delta_{31P} = 25.4 - 37.5$ ppm) as compared to the free ligand ($\delta_{31P} = 2.8$ ppm; see Table S1-1, Supporting Information) showing for the rhodium complexes additional couplings of ¹J_{RhP} = 156.4 Hz (**2**) and ¹J_{RhP} = 122.7 Hz (**3**).



Scheme 2. Synthesis of 1-5

Single crystals of all multimetallic complexes suitable for structure determination by X-ray diffraction were obtained and confirmed the identities of the products (Figure 1). The rhodium and iridium atoms in **2**, **3**, and **4** are coordinated in the expected square-planar geometry. The M–P distances are in accordance with those of similar structures. The gold atom in **5** exhibits the expected linear geometry with d(Au-P) = 222.3(4) pm in the normal range. In all structures, the bonding motifs of the ferrocenophane unit are not much influenced upon coordination to a transition metal (see section S2 of the Supporting Information). The distances between the iron atom(s) and the respective transition metal are very similar for **2** (460.0 pm) and **4** (458.7 pm), and are shorter in **3** (450.5 pm) and **5** (433.5 pm).



Figure 1. Molecular structures of the complexes **2–5**. Selected distances (pm): **2**: Fe^{...}Rh 460.0(2), Rh–P 229.8(1); **3**: Fe^{...}Rh (av.) 450.5(1), Rh–P (av.) 231.2(1); **4**: Ir^{...}Fe 458.7(2), Ir–P 229.6(1); **5**: Fe^{...}Au 433.6(2), Au–P 222.3(4). See also section S2 of the Supporting Information.

The electrochemical properties of all title compounds (1-5) were probed with the aid of cyclic voltammetry. The $E^{0}_{1/2}$ values for the iron-centred oxidation (strongly) depend on the coordinated

transition metal fragment. The largest effect is observable when pure ligand 1 ($E^{0}_{1/2} = -0.01$ V) is compared with the gold complex 5 ($E^{0}_{1/2} = 0.44$ V, Figure 2a). For the dinuclear complexes, anodic shifts of the first, iron-centred redox events are observed in the series $1 < 2 \approx 4 < 5$ (Table 1). This trend nicely confirms the electronic communication between the metal atoms in these scaffolds.

Table 1. Ha	alf-wave potentials	, peak potential	differences	and corresponding
i li voluco	of 1 E in CH.CL.V	a Ea/Ea ⁺ (intern	al atopdard)	y = 100 m//c

Ipc/Ipa Values C	of 1-5 IN CH2CI2 VS. FC/FC	(Internal standard); V	= 100 mv/s.
Compound	<i>E</i> ⁰ _{1/2} / V	$\Delta E_{\rm p} / \rm mV$	i _{pc} /i _{pa}
1	-0.01	104	~1
2	0.07 / 0.39	68 / 106	~0.7 / ~1
3	0.13 / 0.30	101 / 106	~1 / ~1
4	0.12 ^{a,b}	96ª	~1ª
5	0.44	99	~1
a 50	. b A a sa sa a la sa a la sa sa sa sa b	succession and and CO	- 0.40.)/hish

^a v = 50 mV/s; ^b A second redox event was observed at $E_{1/2}^0 = 0.48 \text{ V}$, which presumably belongs to the Ir(I)/Ir(II) couple. However, the intensity was found to be much lower (see Section S3).

For some complexes, e.g. **2** (Figure 2), a second redox event was observed at $E_{1/2}^0(2) = 0.39$ V, which was attributed to the Rh(I)/Rh(II) couple, as previously discussed.^[12] It has to be noted, however, that we consequently had to use the electrolyte [NBu₄][Al{OC(CF₃)₃}]^[13] containing a weakly coordinating anion for our studies. Even under these consitions, the first oxidation of **2** at $E_{1/2}^0(1) = 0.07$ V shows only quasi-reversible behaviour with $i_{pc}/i_{pa} \approx 0.7$ and $\Delta E_p = 68$ mV (see also section S3).



Figure 2. (a) Cyclic voltammograms of 1 (green), 5 (red) and 2 (blue) in CH_2Cl_2 vs Fc/Fc⁺; v = 100 mV/s, Pt/[NBu4][Al{OC(CF_3)}]₃]/Ag. (b) Overlaid calculated structures of q3' (fogged background) and q3'⁺ (foreground) and q2 and q2⁺, both including calculated spin density of q3'⁺ and q2⁺ obtained at the B3LYP/def2-TZVP level.

DFT computations were performed on the neutral and cationic rhodium carbonyl complexes [Rh(k¹P-1)(CO)₂Cl]^{0/+} (q3' and q3'+ Scheme 2). The structural changes upon going from q3 to q3'* are relatively small. As expected, the spin density in q3'+ is predominantly located on the Fe atom (Figure 2b). The difference in the Tolman electronic parameters (TEP)^[14] values upon switching the redox-state of **1** in the complex [Rh($\kappa^1 P$ -1)(CO)₂Cl]^{0/+} was calculated to $\Delta TEP^{calc} = 22 \text{ cm}^{-1}$. Previous calculations on the related metalloligand IX (Scheme 1) gave similar values.^[7] As noted before, these calculated TEP changes for the gas-phase species overestimate the effect of changing the redox-state of the ligand by a factor of ca. 2.[7] The qualitative trend to decreasing the donor and/or increasing the acceptor properties of 1 upon oxidation was further confirmed by inspecting the neutral and oxidized form of the 1:2 complex $[Rh(\kappa^1P-1)_2(CO)Cl]^{0/+}$ (q3 and q3⁺, Scheme 2, Figure S5-2). Also

COMMUNICATION

in this case, as for **q2**⁺ (Figure 2), the spin density in **q3**⁺ is predominantly located on the Fe atoms. As expected, the calculated CO stretching frequency considerably change from $v^{calc} = 1970 \text{ cm}^{-1}$ for **q3** to $v^{calc} = 1981 \text{ cm}^{-1}$ for **q3**⁺.^[15] The results prompted us to apply the stimuli-responsive metal complexes in redox-switchable/redox-induced catalysis.

 Table 2.
 Hydrosilylation of terminal alkynes (cf. Scheme 3).
 Product distributions are given for the time at which the substrates are consumed.

 Subsequent isomerisation are not considered.
 Subsequent.
 Subsequent.
 Subsequent.

	alkyne	silane	cat.	mol	t	conv.	β-	β-	α	poly
	(R' =)	HSiR₃		%	[min.]	[%]	(Z)	(E)		
		(R =)								
	1 H	Me ₂ Ph	2	1.0	80	>99	52	40 ^b	<1	7
2	2 H	Me ₂ Ph	2 +	1.0	5	>99	0	40	14	45
:	3 H	Me ₂ Ph	2 ⁺	0.25	130	>99	0	65	6	28
4	4 4-MeO	Me ₂ Ph	2	1.0	90	95	48	46	0	6
!	5 4-MeO	Me ₂ Ph	2 +	0.25	15	>99	32	35	0	32
(6 4-CF ₄	Me ₂ Ph	2	1.0	65	>99°	48	44 ^b	5	0
7	7 4-CF ₄	Me ₂ Ph	2 ⁺	1.0	10	>99°	0	59	41	0
8	8 4-CF4	Me ₂ Ph	2 ⁺	0.25	105	86°	12	74	14	0
9	9 H	Et ₃	2	1.0	310	98	42	32	<1	25
1	0 H	Et ₃	2 ⁺	0.5	165	92	0	95	5	0
1	1 H	Me(OEt) ₂	2	1.0	130	>99	29	43 ^b	<1	27
1	2 H	Me(OEt) ₂	2⁺	0.25	105	96	0	95	5	0

^a Determined by ¹H NMR spectroscopy (no activity with pure ligand or pure oxidising reagent; no metallopolymer formation during catalysis (³¹P NMR spectroscopy); activity remains after adding a second batch of alkyne + silane). c(alkynes) = 0.02 – 0.05 mmol/ml. ^b Isomerisation β -(Z) $\rightarrow \beta$ -(E) is observed with time (Table S4-1). ^c The products precipitate during the reaction.

The application of complexes featuring [*n*]metallocenophanes as ligands in redox-switchable catalysis is – to the best of our knowledge – limited to one report on olefin metathesis polymerisation catalysts based on the diaminocarbene-[3]ferrocenophane **VIII** by the group of Bielawski.^[16] In order to investigate the applicability of the bimetallic complexes reported herein in this area, we have studied the hydrosilylation^[17] of terminal alkynes and silanes using **2** and *in situ* generated **2**^{+[18]} as catalysts. All reactions were performed in CD₂Cl₂ at room temperature and were monitored by ¹H NMR spectroscopy. Control reactions on gram scale were also performed (section S4).



Scheme 3. Overview of the hydrosilylation reactions performed in this study including a possible product distribution (those which have not been observed are shown in grey).

In general, hydrosilylation reactions^[19] of alkynes can lead to a mixture of three isomers: the geminal product α and the β -(Z) and β -(E) alkenes alongside other by-products (Scheme 3). Neutral and cationic Rh(I) complexes are known to favour the β -(Z) product, while the geminal product (α) is formed only in little amounts or not at all (for a more detailed discussion of mechanistic aspects, see below).^[20] **2** was found to be an efficient catalyst for the hydrosilylation of terminal alkynes with periods after which 50% of the alkyne was consumed (t_{50}) between 17 and 58 minutes. The main products were the respective β -(Z) and β -(E) alkenes. The competing reaction was found to be the polymerisation of the alkyne, which was obtained

in varying amounts (between 6 and 27%). Table 2 shows an overview of the tested reactions alongside the collected activity and selectivity data (*cf.* Scheme 3).

It has to be noted that in some cases the β -products underwent isomerisation,^[21] which led to a high yield of the respective β -(E) alkene over time (Section S4, Supporting Information). However, we will discuss selectivity issues on the basis of the preferred kinetic products only. 4-methoxyphenyl acetylene was the only alkyne from the tested ones, which was not consumed completely (about 5% remained left) and needed an initiating phase (see Figure S4-1). The obtained β -vinyl silanes seemingly has a positive effect on the reaction rate. Generally, the rates were found to be predominantly affected by the substituents on the alkyne. A detailed analysis of the kinetics will be performed in a separate study.

In order to elucidate if the oxidation of the iron atom in **2** has an effect on the reaction rates and/or the product distribution, one equivalent (based on **2**) of the acetyl ferrocenium salt [FeCp(C₅H₄COMe)][Al{OC(CF₃)₃}]₄] was added to the catalyst (mixture of **2** and the oxidation reagent are referred to as **2**⁺). This oxidation reagent was specifically chosen due to its redox potential in CH₂Cl₂ ($E^{0}_{1/2} = 0.27$ V). This value lies between the determined half-wave potentials of **2** with $E^{0}_{1/2}(1) = 0.07$ V and $E^{0}_{1/2}(2) = 0.39$ V (Figure 2) and should therefore only oxidise the iron atom.

All reactions were greatly accelerated with 2^+ as a catalyst as compared to 2. The rate accelerating effect is illustrated in some reaction profiles (Figure S4-1). For instance, the reaction of phenyl acetylene with HSiMe₂Ph was finished after only 5 minutes using 1 mol% of 2^+ (80 minutes for 2, entries 1 and 2 in Table 2). Similar conversion rates have been obtained for phenyl acetylene and HSiMe₂Ph using only 0.25 mol% of 2^+ instead of 1 mol% of 2 (entries 3 and 1, Table 2; Figure S4-1). The rate accelerating effect is slightly less pronounced for the substrate containing the electron withdrawing CF₃-substituent (entries 6-8) The electron rich 4-MeO-C₆H₄C=CH alkynes, however, is converted even faster using 0.25mol% 2^+ (15 min.) instead of 1 mol% 2 (90 min., entries 5 and 4). A similar trend is observed for other silanes (entries 9–12).

Even more importantly, the selectivity of the catalysis considerably changed and a very different product distribution was obtained for 2 and 2+ (Table 2). While the reaction of PhC=CH and HSiMe₂Ph catalysed by **2** led to mixture of the β -(E)- and β -(Z)-alkene (40% and 52%), no β -(Z)-isomer is formed with 2^+ while increased polyphenyl acetylene formation is observed. The selectivity is further increased at lower catalyst loadings (0.25 mol%, 65% β -(E), entry 3). Although the selectivity effect is much less pronounced for the substrate 4-MeO-C₆H₄C=CH (entries 4 and 5), the electron poor alkyne 4- CF_4 - C_6H_4C =CH again gave no β -(Z)-alkene with HSiMe₂Ph and 1 mol% 2⁺ (only 12 % with 0.25 mol% 2⁺, entries 7 and 8). Only for this substrate also the α product is formed in considerable amounts (41% for 1 mol%; 14% for 0.25 mol%). The most impressive results, however, were obtained with PhC=CH and the two silanes HSiEt₃ and HSiMe(OEt)₂ (entries 9-12). While 2 gave in each case a typical product distribution for Rh-catalysed hydrosilylations, 2^+ almost exclusively produced the β -(E)-alkene (95% in each case, entries 10 and 12).

The widely accepted mechanism used to describe platinumcatalysed hydrosilylation reactions is the Chalk-Harrod mechanism (C.H., Scheme 4),^[19,20] which involves key steps such as the oxidative addition of silanes $HSiR_3$, alkyne binding, insertion of the latter into the Pt–H bond, and reductive

COMMUNICATION

elimination by Si–C bond formation and elimination of the β -(E) vinylsilane. Since some occurrences, such as the formation of alkynyl silanes (Scheme 4), cannot be explained by this mechanism, the so-called modified Chalk-Harrod (m.C.H.) mechanism was proposed later. In the m.C.H. mechanism, the alkyne inserts into the M–Si bond to furnish a metal alkenyl intermediate. The geminal α product or β -(Z) vinylsilane are considered to form after isomerisation of the metal alkenyl intermediate.



 $\label{eq:Scheme 4. Chalk-Harrod (A) and modified Chalk-Harrod (B) mechanism for the hydrosilylation of alkynes.$

In contrast to platinum, rhodium-catalysed hydrosilylation reactions occur preferentially along the m.C.H. mechanism and therefore exhibits different selectivities. In a seminal paper, Sakaki and co-workers investigated the elementary steps of both mechanistic variants in the rhodium-catalysed hydrosilylation of ethylene by quantum chemical calculations.^[22] It was concluded that the rate-determining step in the C.H. mechanism is the Si–C reductive elimination (114.6 kJ mol⁻¹ at DFT level). The ethylene insertion into the Rh–H bond in the classical C.H. mechanism is basically barrier-free (<1 kJ mol⁻¹). Contrary to this, the rate-determining step of the m.C.H. mechanism is either ethylene insertion into the Rh–Si bond (56.5 kJ mol⁻¹) or the oxidative addition of the silane (65.7 kJ mol⁻¹), depending on the level of theory. Overall, the m.C.H. mechanism is therefore more favourable in Rh-catalysed hydrosilylations.



We speculated that in our case the introduction of an additional positive charge on the metalloligand lowers the activation barrier of the Si–C reductive elimination to such an extend that the classical C.H. mechanism becomes favourable for the rhodium catalyst **2**⁺. Indeed, DFT calculations (BP86/def-SV(P) and {B3LYP/def2-TZVPP}) provided clear evidence: the activation barrier for the reductive elimination step was found to be considerable smaller (64.4 kJ {66.7} mol⁻¹) for **2**⁺ as compared to **2** (105.5 {82.1} kJ mol⁻¹, Scheme 5; see also Table S5-1). Our calculations also predict that going form the starting to the transition state both the positive charge and the spin density in **2**⁺ is significantly shifted to the rhodium atom (*q*(Rh)^{Start} = 0.13, *q*(Rh)^{TS} = 0.46; *sd*(Rh)^{Start} = 0.00, *sd*(Rh)^{TS} = 0.84; all for B3LYP/def2-TZVPP).

Overall, the observed effects in redox-induced catalysis^[23] can be explained as follows: the oxidation of the iron atom in the metalloligand causes an additional positive charge on the rhodium atom. Being in the formal oxidation state +3 before the reductive elimination step, the additional charge lowers the activation barrier to re-generate the +1 oxidation state of Rh. This cooperative "oxidatively induced reductive elimination" step obviously provides the key to a different catalytic cycle and thus to both a higher catalytic activity and, in most cases, a markedly different selectivity.

Experimental Section

Experimental Details: See the Supporting Information.

Acknowledgements

We acknowledge financial support from the DFG-funded transregional collaborative research centre SFB/TRR 88 "Cooperative effects in homo- and heterometallic complexes (3MET)" (projects B1 and B4). We thank Wolfram Feuerstein for calculating the *g* tensor of 2^* .

Keywords: Redox-switchable catalysis, [1]ferrocenophane, cooperative effects, bimetallic complexes, metalloligand

References

- (a) A. M. Allgeier, C. A. Mirkin, *Angew. Chem., Int. Ed.* **1998**, *37*, 894; (b)
 V. Lyaskovskyy, B. de Bruin, *ACS Catal.* **2012**, *2*, 270; (c) O. R. Luca, C.
 H. Crabtree, *Chem. Soc. Rev.* **2013**, *42*, 1440; (d) V. Blanco, D. A. Leigh,
 V. Marcos, *Chem. Soc. Rev.* **2015**, *44*, 5341; (e) V. K. K. Praneeth, M. R.
 Ringenberg, T. R. Ward, *Angew. Chem. Int. Ed.* **2012**, *51*, 10228.
- 2 I. M. Lorkovic, R. R. Duff, M. S. Wrighton, J. Am. Chem. Soc. 1995, 117, 3617.
- 3 Reviews: (a) S. M. Guillaume, E. Kirillov, Y. Sarazin, J.-F. Carpentier, *Chem. Eur. J.* **2015**, *21*, 7988; (b) A. J. Teator, D. N. Lastovickova, C. W. Bielawski, *Chem. Rev.* **2016**, *116*, 1969.
- 4 Selected examples: (a) C. K. A. Gregson, V. C. Gibson, N. J. Long, E. L. Marshall, P. J. Oxford, A. J. P. White, *J. Am. Chem. Soc.* 2006, *128*, 7410; (b) X. Wang, A. Thevenon, J. L. Brosmer, I. Yu, S. I. Khan, P. Mehrkhodavandi, P. L. Diaconescu, *J. Am. Chem. Soc.* 2014, *136*, 11264.
- (a) L. Hettmanczyk, S. Manck, C. Hoyer, S. Hohloch, B. Sarkar, *Chem. Commun.* 2015, *51*, 10949; (b) S. Ibáñez, M. Poyatos, L. N. Dawe, D. Gusev, E. Peris, *Organometallics* 2016, *35*, 2747; (c) L. Hettmanczyk, L. Suntrup, S. Klenk, C. Hoyer, B. Sarkar, *Chem. Eur. J.* 2017, *23*, 576; for closely related work, see (d) P. Neumann, H. Dib, A.-M. Caminade, E. Hey-Hawkins, *Angew. Chem. Int. Ed.* 2015, *54*, 311; (e) K. Arumugam, C. D. Varnado, Jr., S. Sproules, V. M. Lynch, C.W. Bielawski, *Chem. Eur. J.* 2013, *19*, 10866; (f) M. Süßner, H. Plenio, *Angew. Chem. Int. Ed.* 2005, *44*, 6885.
- (a) S. González-Gallardo, I. Kuzu, P. Ona-Burgos, T. Wolfer, C. Wang, K. W. Klinkhammer, W. Klopper, S. Bräse, F. Breher, *Organometallics* 2014, 33, 941; (b) S. Styra, S. González-Gallardo, F. Armbruster, P. Ona-Burgos, E. Moos, M. Vonderach, P. Weis, O. Hampe, A. Gren, Y. Schmitt, M. Gerhards, F. Menges, M. Gaffga, G. Niedner-Schatteburg, F. Breher, *Chem. Eur. J.* 2013, *19*, 8436.
- 7 F. Walz, E. Moos, D. Garnier, R. Köppe, C. E. Anson, F. Breher, *Chem. Eur. J.* 2017, 23, 1173.
- Recent reviews on strained sandwich compounds: (a) D. E. Herbert, U. F. J. Mayer, I. Manners, Angew. Chem. Int. Ed. 2007, 46, 5060; (b) M. Tamm, Chem. Commun. 2008, 3089; (c) H. Braunschweig, T. Kupfer, Acc. Chem. Res. 2010, 43, 455; (d) H. Bhattacharjee, J. Müller, Coord. Chem. Rev. 2016, 314, 114. Selected examples on [1]phosphaferrocenophanes: (e) E. K. Sarbisheh, J. C. Green and J. Müller,

COMMUNICATION

Organometallics **2014**, *33*, 3508; (f) M. Herberhold, F. Hertel, W. Milius, B. Wrackmeyer, J. Organomet. Chem. **1999**, *582*, 352; (g) T. Mizuta, Y. Imamura, K. Miyoshi, J. Am. Chem. Soc. **2003**, *125*, 2068; (h) S. K. Patra, G. R. Whittell, S. Nagiah, C.-L. Ho, W.-Y. Wong, I. Manners, Chem. Eur. J. **2010**, *16*, 3240; (i) I. R. Butler, W. R. Cullen, F. W. B. Einstein, S. J. Rettig, A. J. Willis, Organometallics **1983**, *2*, 128; (j) H. Brunner, J. Klankermayer, M. Zabel, J. Organomet. Chem. **2000**, *601*, 211; (k) D. Seyferth, H. P. Withers, J. Organomet. Chem. **1980**, *185*, C1; (l) A. G. Osborne, R. H. Whitely, J. Organomet. Chem. **1980**, *193*, 345.

- 9 Selected reviews on ferrocene-based ligands: (a) U. Siemeling, Eur. J. Inorg. Chem. 2012, 3523; (b) D. Astruc, Eur. J. Inorg. Chem. 2017, 6.
- (a) J. Chmela, M. E. Harding, D. Matioszek, C. E. Anson, F. Breher, W. Klopper, *ChemPhysChem* 2016, *17*, 37; (b) A. Feyrer, F. Breher, *Inorg. Chem. Front.* 2017, DOI: 10.1039/c7qi00125h.
- 11 The reaction of 2 with CO was performed in a J. Young NMR tube. ¹H and ³¹P NMR spectroscopic monitoring of the reaction revealed that 3 is formed very fast; the spectra of the reaction mixture directly showed only signals corresponding to 3 and free cod. Even though the other product containing the missing equivalent of rhodium was not identified, it is reasonable to assume that [Rh(CO)₂Cl]₂ was formed. Similar ligand exchange processes have been observed before: See, e.g. (a) F. Lorenzini, B. O. Patrick, B. R. James, *Dalton Trans.* 2007, 3224; see also (b) S. Chen, E. Manoury, R. Poli, *Eur. J. Inorg. Chem.* 2014, 5820.
- 12 (a) D. M. Khramov, E. L. Rosen, V. M. Lynch, C. W. Bielawski, Angew. Chem. Int. Ed. 2008, 47, 2267; see also (b) U. Siemeling, C. Färber, C. Bruhn, Chem. Commun. 2009, 98.
- (a) I. Raabe K. Wagner, K. Guttsche, M. Wang, M. Grätzel, G. Santiso-Quiñonoes, I. Krossing, *Chem. Eur. J.* 2009, *15*, 1966; (b) W. E. Geiger, F. Barrière, *Acc. Chem. Res.* 2010, *43*, 1030.
- 14 (a) C. A. Tolman, Chem. Rev. 1977, 77, 313; (b) D. J. Nelson, S. P. Nolan, Chem. Soc. Rev. 2013, 42, 6723.
- 15 The computed vibrational frequencies were scaled by F = 0.9956 (BP86/def2-SVP): M. K. Kesharwani, B. Brauer, J. M. L. Martin, J. Phys. Chem. A 2015, 119, 1701.
- 16 C. D. Varnado, Jr., E. L. Rosen, M. S. Collins, V. M. Lynch, C. W. Bielwaski, *Dalton Trans.* 2013, 42, 13251.
- Another rare example on redox-switchable hydroelementation catalysis:
 S. M. Shepard, P. L. Diaconescu, *Organometallics* 2016, 35, 2446.
- 18 All attempts to prepare the cationic complexes, *e.g.* **2**⁺, on a preparative scale have not yet been successful. Although EPR spectroscopic investigations on in situ generated **2**⁺ have been performed (cw X-band, frozen solution, 100 K), no clear results have been obtained. While CH₂Cl₂ solutions were found to be EPR silent, only a very weak EPR signal was observed in THF, which was not reproducible. DFT calculations on **2**⁺ (see Section S5) indicated axial anisotropy with the principle g values: $g_1 = 2.028$, $g_2 = 2.030$, $g_3 = 2.337$. The much lower g anisotropy of **2**⁺ as compared to ferrocenium (Fc⁺, $g_\perp = 1.30$, $g_{\parallel} = 4.36$, see: R. Prins, F. J Reinders, *J. Am. Chem. Soc.* **1969**, *91*, 4929) can be attributed to its lower symmetry (C_{2V} or lower vs. D_{5d} or D_{5h}), which causes a lifting of the orbital degeneracy. For a discussion on a closely related compound, see e.g. H. Braunschweig, F. Breher, M. Kaupp, M. Groß, T. Kupfer, D. Nied, K. Radacki, S. Schinzel, *Organometallics* **2008**, *27*, 6427.
- 19 (a) A. K. Roy, Adv. Organomet. Chem. 2008, 55, 1; (b) D. Troegel, J. Stohrer, Coord. Chem. Rev. 2011, 255, 1440.
- Selected examples: (a) M. V. Jiménez, J. J. Pérez-Torrente, M. I. Bartolomé, V. Gierz, F. J. Lahoz, L. A. Oro, *Organometallics* 2008, 27, 224; (b) M. Iglesias, M. Aliaga-Lavrijsen, P. J. Sanz Miguel, F. J. Fernández-Alvarez, J. J. Pérez-Torrente, L. A. Oro, *Adv. Synth. Catal.* 2015, 357, 350; (c) L. Busetto, M. C. Cassani, C. Femoni, M. Mancinelli, A. Mazzanti, R. Mazzoni, G. Solinas, *Organometallics* 2011, 30, 5258.
- 21 M. F. Lappert, R. K. Maskell, J. Organomet. Chem. 1984, 264, 217.
- 22 S. Sakaki, M. Sumimoto, M. Fukuhara, M. Sugimoto, H. Fujimoto, S. Matsuzaki, Organometallics, 2002, 21, 3788.
- 23 Although the term "redox-switchable catalysis" is a common description in the literature, one referee of the manuscript argued that, in our case, the term "redox-induced catalysis" might be more appropriate since the reaction can be controlled in only one direction and was not/cannot be brought back to the starting point. We highly appreciate this helpful comment.

COMMUNICATION

Entry for the Table of Contents

COMMUNICATION



Redox-switchable catalysis: Bimetallic complexes of a [1]phosphaferrocenophane are reported featuring a good electronic communication between the metal atoms. A rhodium(I) complex (Figure) was employed as redox-active catalyst in the hydrosilylation of terminal alkynes. Oxidatively induced reductive elimination facilitates higher activity and markedly different selectivity for the oxidised complex

Alexander Feyrer, Markus Armbruster, Karin Fink, and Frank Breher*

Page No. – Page No.

Metal Complexes of a Redox-Active [1]Phosphaferrocenophane: Structures, Electrochemistry and Redox-Induced Catalysis