Multistimuli-Responsive [3]Dioxaphosphapheroconnophanes with Orthogonal Switches

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Abstract: Novel multistimuli-responsive phosphine ligands comprising a redox-active [3]dioxaphosphapheroconnophane backbone and a P-bound imidazolin-2-ylidnamino entity that allows switching by protonation are reported. Investigation of the corresponding metal complexes and their redox behaviour are reported and show the sensitivity of the system towards protonation and metal coordination. The experimental findings are supported by DFT calculations. Protonation and oxidation events are applied in Rh-catalysed hydrosilylations and demonstrate a remarkable influence on reactivity and/or selectivity.

In recent years, the development of stimuli-responsive ligands and their coordination chemistry has garnered significant interest from the scientific research community. One of the main goals of this scientific branch is the ability to control multiple catalytic processes with a single active molecule, of which the activity can be altered by applying stimuli in a specific order. Efforts in this direction have led to the development of systems, where an (ideally reversible) change of the ligating properties of the ligand can be induced by external stimuli such as irradiation with light, protonation or redox-switching.[1] The donating capabilities of such ligands can thus be significantly altered and are usually investigated by measurement of the Tolman electronic parameter (TEP).[12] Redox-active systems are most often based on ferroceny (Fc)-containing mono- or multidentate ligands. In this context, ferrocenyl-decorated phosphines, N-heterocyclic carbenes (NHCs) and mesoionic carbenes (MICs) usually show a TEP change of approximately 7.4–12.7 cm⁻¹ upon oxidation of the ferrocene unit.[3-6] The ferrocene (Fc)-based oxidation/reduction not only “switches” the σ-donor and π-acceptor properties of the ligand itself, but can further influence the properties of a coordinated metal. Investigations on catalytically active systems based on such multimetallic complexes have shown that changes can significantly influence the activity of the catalysts as well as its selectivity. This has been demonstrated in a variety of reactions such as ring-opening polymerization,[7,8] hydroamination,[9,10] or hydrosilylation,[9,11] among others.[10b]

The ability to switch the ligating properties of a ligand by protonation can be achieved by introduction of a Brønsted-basic pendent group. The groups of Glorius and Dielmann synthesized such systems based on an anionic enolate-imidazolinylidine ligand[12] and imidazoline-2-ylidnaminophosphines (IAPs),[13] respectively (Figure 1). The enolate-imidazolinylidine-based system exhibits a TEP change of 14 cm⁻¹, while the IAPs show an increase of approximately 22 cm⁻¹ per protonation step, allowing an increase of up to 43 cm⁻¹ upon twofold protonation. Further examples for stimuli-responsive ligands include external triggers such as UV-light[14] or coordination events.[15]

With these recent developments on multifunctional ligands[16] in mind, our groups became interested in combining the properties of redox-active and proton-sensitive systems, as it has already been shown that phosphoramidites with a ferrocenyl backbone are chemically accessible.[17] This would potentially allow for orthogonal switching by different stimuli, thus giving chemists a new tool to adapt towards reaction conditions in redox-switchable catalysis.

The dioxaphosphapheroconnophane-based[18] title compounds L1 and L2 (Scheme 1) were obtained by treating the known 1,1′-ferrocenediyl[19] and the corresponding imidazoline-2-ylidnamino dichlorophosphines (L1: R=IPr, L2: R=Mes) as yellow air- and moisture-sensitive crystalline solids in 50 and 44 % isolated yield, respectively (Scheme 1). The 31P NMR signals are observed at 142 and 156 ppm for L1 and L2, respectively, which is comparable to other [3]dioxaphosphapheroconnophanes.[10a]

The molecular structures were determined and are shown in Figure 2. In comparison to other [3]dioxaphosphapheroconnophanes, the distances between the iron atom and the phosphorus atom are increased. The known compounds in
which the phosphorus atom bears a tert-butyl- or a terphenyl-
(2,6-Mes$_2$C$_6$H$_3$) moiety\cite{footnote10} show distances of $d = 330.8$ and
337.6 pm, respectively. For the proligands $L_1$ and $L_2$, values of
343.7 and 358.7 pm, respectively, were found.

For direct measurement of the TEP values, and to compare
the coordination behaviour of the ligands with previously
reported phosphaferrocenophanes, we decided to focus on the
synthesis of the corresponding Ni, Au and Rh compounds.

The metal complexes $[L_1 \text{Ni(CO)}_3]$ (1), $[L_1 \text{AuCl}]$ (2), and $[L_1 \text{Rh}
(cod)\text{Cl}]$ (3) for $L_1$ and $[L_2 \text{Ni(CO)}_3]$ (4) and $[L_2 \text{Rh(cod)Cl}]$ (5) for
$L_2$ were prepared by reacting the free ligands with a suitable
metal precursor in THF or toluene and were subsequently
isolated by crystallization from concentrated $n$-hexane (1 and 4)
or toluene (2, 3 and 5) solutions (Scheme 2). Yields varied
around 60% for the rhodium and gold compounds, while the
nickel compounds could be obtained in almost quantitative
yield.

Molecular structures of 1–5 were determined from single
crystals and are shown in Figure 3. Whereas the distances in
the ligand moiety of $L_2$ do not change significantly upon coordina-
tion of a metal fragment, a medium increase can be observed
in the case of $L_1$. Complexes 1 and 3 show a lengthening of the
Fe···P distance of 11.3 and 11.8 pm, respectively. This is less
pronounced in the gold(I) complex 2, which can be explained
by the steric demands of the coordinated metals, which is the
lowest for 2. However, compared to the other metal complexes
of $L_1$, the gold(I) complex shows a shortening of the P–N
distance by 3.9 pm, and the N–C$_{ipso}$ distance is lengthened by

perfectly planar (Table 1), with the dihedral angle between the character of the N bond strength, which in turn decreases the double bond transferred from the phosphorus atom, thereby increasing the P nature of the {AuCl} fragment more electron density is trans-

4.3 pm. We believe that due to the high electron-withdrawing nature of the (AuCl) fragment more electron density is transferred from the phosphorus atom, thereby increasing the P–N bond strength, which in turn decreases the double bond character of the N–C^\text{ipso} bond.

While the proligands L1 and L2 behave relatively similar upon coordination, one significant difference can be observed. For metal complexes of L1, the M–P–N–C^\text{ipso} fragment is almost perfectly planar (Table 1), with the dihedral angle between the M–P–N and the P–N–C^\text{ipso} planes being between 0° and 7°. For metal complexes of L2, the torsion angle between the M–P–N and the P–N–C^\text{ipso} planes is around ~120°, with the imidazolium moiety sticking out of the M–P–N plane.

The TEP values of L1 (2068.5 cm\(^{-1}\)) and L2 (2064 cm\(^{-1}\)) were determined from the nickel(0) complexes 1 and 4. The ligands are thus comparable with PPh\(_3\) or PBz\(_2\) and are better donors than the phosphate ligand P(O–Pr)\(_2\)Ph (TEP values of 2068, 2066 and 2072 cm\(^{-1}\), respectively).\(^{[2]}\)

Attempts to oxidize L1 with AgOTf surprisingly yielded a dimeric compound (6, Figure 4), in which two ligands and two silver atoms form a six-membered ring. This structural motif represents an unusual coordination pattern for IAP-type ligands. The silver atoms are coordinated by one phosphorus atom, one nitrogen atom and the triflate ion. The metal complex does not appear to dissociate into monomeric units in solution, as can be deduced from the \(^{13}\)P NMR spectrum. The doublets resulting from the \(\text{J}(^{13}\text{P}–107\text{Ag})\) and \(\text{J}(^{13}\text{P}–109\text{Ag})\) couplings are further split as result of the \(\text{J}^2\) coupling to the second silver atom (Figure S30 in the Supporting Information).

Protonation of L1 with [H(OEt\(_2\))]\(_2\)[Al(OC(CF\(_3\)))\(_3\)] in THF furnished the protonated compound L1H\(^+\). In the crystal structure (Figure S5), hydrogen bonding of the N-bound proton towards one molecule of THF can be observed. The P–N and N–C^\text{ipso} distances are both increased by 7.8 and 6.6 pm, respectively, as compared to L1 (Table 2). This is not surprising, as protonation decreases the electron density on the nitrogen atom, which in turn leads to a weakening of the aforementioned bonds.

The \(^1\)H NMR spectrum of L1H\(^+\) in [D\(_6\)]THF shows signals for two isomers clearly visible by two sets for the isopropyl C–H group, the ratio of which are roughly 3:1. We believe that this arises from coordination and de-coordination of the THF moiety and does not indicate decomposition as the ratio does not change even after several weeks. When protonation was carried out in situ in an NMR test tube, at first only the major isomer could be observed. The minor isomer formed over the course of three days after which the ratio does not change anymore. Furthermore, after addition of DBU, both signals for the isopropyl C–H group disappear and only one set corresponding to the deprotonated free proligand L1 can be observed.

| Table 2. Selected distances [pm] and angles [°] of L1, 2, L1H\(^+\) and 2H\(^+\). |
|------------------|------------------|------------------|------------------|------------------|
| \(d(\text{Fe–P})\) | \(d(\text{P–N})\) | \(d(\text{N–C}^{\text{ipso}})\) | \(d(\text{P–M})\) | \(|\omega|\) (M–P–N–C^\text{ipso}) |
| L1\(^+\) | 343.7 | 159.7 | 131.1 | – | – |
| 2 | 347.8 | 155.8 | 135.4 | 221.2 | 0 |
| 2H\(^+\) | 340.0 | 162.1 | 141.5 | 219.7 | 1.0 |

[a] Averages of two molecules in the asymmetric unit. [b] Averages of three molecules in the asymmetric unit.
The protonated gold(I) complex 2H\textsuperscript{+} can be prepared by treating L1H\textsuperscript{+} with [{(tht)AuCl} or by protonating 2 with [H(OEt)\textsubscript{2}][AuOC(CF\textsubscript{3})\textsubscript{3}]\textsubscript{2}\textsuperscript{-} (Scheme 3; isolated yields: 62\% and 95\% respectively). Similarly to L1H\textsuperscript{+}, the proton is again engaged in a hydrogen bond with the oxygen atom of THF (Figure 5). The P–N and N–Cipso distances increase by 6.3 pm and 6.1 pm, respectively, which underlines the effects observed for L1H\textsuperscript{+}. Furthermore, the Fe–P distance decreases by 7.8 to 340 pm, which is comparable to the previously investigated gold(I) complexes of [3]-dioxaphosphaferrrocenophanes.\textsuperscript{[10]}

In THF solution, the 1H NMR spectrum shows only a set of signals even after several days, thus indicating that only one isomer is present. In contrast to all other compounds investigated, the protons of the methyl moieties in the imidazolyl residue are no longer equal and can be observed as two singlets; this shows that free rotation around the P–N or N–Cipso bonds is hindered.

In situ protonation of nickel tricarbonyl complex 1 to furnish 1H\textsuperscript{+} gives a TEP of 2092 cm\textsuperscript{-1} with an increase of ΔTEP = +23.5 cm\textsuperscript{-1} as compared to 1. These observations are similar to the results of the protonation of IAPs, which led to an increase of ΔTEP = +22.5 cm\textsuperscript{-1}.\textsuperscript{[13]} However, further characterization of protonated 1H\textsuperscript{+} was not possible due to fast decomposition in solution.

Protonation of L2 and, independently, its nickel complex 4 also lead to decomposition, which can be observed by the disappearance of the CO bands in the IR spectrum. We believe that this can be attributed to the greater steric hindrance on the nitrogen atom. As the proton is bound to one or two molecules of the ethereal solvent, the imino group is far less accessible than the phosphinate group, which might give rise to protonation of the less robust O–P–O moiety.

The redox behaviour of the phosphaferrrocenophanes and their metal complexes were investigated with the aid of cyclic voltammetry (Table 3, Figure 6). The \(E_{1/2}'\) values for the Fe-centred oxidation (see below) strongly depend on the coordinated transition metal fragment and/or the protonation of the ligand. The redox potential of the free ligands (\(E_{1/2}' = -160\) mV (L1) and \(-150\) mV (L2)) vs. Fe(II)/Fe\textsuperscript{+} in CH\textsubscript{2}Cl\textsubscript{2} are cathodically shifted by approximately 150–200 mV in comparison to other [3]-dioxaphosphaferrrocenophanes,\textsuperscript{[17]} confirming the electron donating capabilities of the imidazolin-2-ylidenamino moiety. Coordination of a [AuCl] fragment (2, entry 5) leads to an anodic shift of \(+350\) mV, which is slightly more pronounced as compared to previous studies from our laboratory\textsuperscript{[8]} showing coordination shifts for [AuCl] complexes of about \(+270–300\) mV. Protonation also has a dramatic influence on the redox potential of the ferrocene moiety (Entries 2 and 6). For the protonated free ligand L1H\textsuperscript{+}, the redox potential is shifted by
+ 540 mV as compared to L1. This observation is further supported by density functional theory (DFT) calculations at the B3LYP/def-2-TZVP level of theory. Compared to L1, the energies of the iron-centred HOMO is lowered by 0.3559 eV for the \{Ni(CO)\}_3 complex. The experimental redox potential shift was found to be \( \Delta E_{\text{exp}} = +70 \) mV (entries 2 and 3). For the protonated ligand L1H+, a lowering of the HOMO of 2.8734 eV was calculated, which would translate into a calculated redox potential shift of about 610 mV. Indeed, cyclic voltammetry studies on \([\text{L1Ni(CO)}_3\text{H}]^+\) gave \( E^{1/2} = +480 \) mV and, thus, \( \Delta E_{\text{exp}} = +630 \) mV against L1.

The effect of protonation on the redox potential can be observed by NMR spectroscopy (Scheme 4). Due to its lower redox potential than ferrocene, oxidation of L1 with \([\text{Cp}_2\text{Fe}][\text{B(C}_6\text{F}_5\text{)}_4]\) leads to disappearance of the signals for L1, and only ferrocene can be observed in the \(^1\text{H}\) NMR spectrum. However, since the protonated proligand L1H+ is harder to oxidize than ferrocene, after addition of \([\text{H(OEt}_2)_2][\text{AlOC(CF}_3\text{)}_3)_4]\), the ferrocene signal at \( \delta_{\text{H}} = 4.0 \) ppm disappears again and signals corresponding to L1H+ appear (Scheme 4).

Attempts to isolate the oxidized ligands and metal complexes always gave reddish-brown, paramagnetic oils, no matter the chosen oxidant or counterion. However, reacting 1 with a substoichiometric amount of \([\text{CpFe(C}_5\text{H}_4\text{OMe})][\text{PF}_6]\) gave rise to a new CO band in the IR spectrum. The latter is observed at 2089 cm\(^{-1}\) (Figure S54), indicating a change of the TEP by case of L1, the calculations also show, that while the HOMO is predominantly centred on the iron atom, a significant portion is also located on the nitrogen and phosphorus atoms, whereas in the case of L1H+, the HOMO is basically completely centred on the iron atom (Figure 7). Based on these findings we expected an additive effect upon coordination of a \{Ni(CO)\}_3 fragment (\( \Delta E_{\text{exp}} = +70 \) mV) and concomitant protonation (\( \Delta E_{\text{exp}} = +540 \) mV) to furnish a potential shift of about 610 mV. The effect of protonation on the redox potential can be observed by NMR spectroscopy (Scheme 4). Due to its lower redox potential than ferrocene, oxidation of L1 with \([\text{Cp}_2\text{Fe}][\text{B(C}_6\text{F}_5\text{)}_4]\) leads to disappearance of the signals for L1, and only ferrocene can be observed in the \(^1\text{H}\) NMR spectrum. However, since the protonated proligand L1H+ is harder to oxidize than ferrocene, after addition of \([\text{H(OEt}_2)_2][\text{AlOC(CF}_3\text{)}_3)_4]\), the ferrocene signal at \( \delta_{\text{H}} = 4.0 \) ppm disappears again and signals corresponding to L1H+ appear (Scheme 4).

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Upon addition of decamethyl ferrocene, the intensity of the band is drastically reduced, which underlines the reversibility of the redox process. To further support this finding, we reacted 1 with an oxidant in situ in an NMR tube and, subsequently, with Fc*, which refurnishes the original NMR of 1 (Figure S56).

To demonstrate the influence on reactivity of the metal complexes by applying oxidation or protonation events, we decided to investigate the rhodium-catalysed hydrosilylation of alkynes (Scheme 5). Our research group has already demonstrated that redox-switching of rhodium complexes with [1]-phosphaferrocenophanes has a profound influence on the rate of the reaction and the selectivity. We have particularly chosen this rather “slow” catalytic system in order to obtain unaffected results by polymerization reactions, which are known for similar catalytic systems. When the rhodium complex [L1Rh(cod)Cl] (3) was employed as precatalyst for the conversion of 1-hexyne with triethyl silane (Table 4, entry 1), the β(E) and β(Z) isomers were found to be the main products, as expected (Figure S51). Although the addition of a proton source (entry 2) does not influence the total rate of conversion, it drastically influences the selectivity, that is, only the β(E) isomer, together with a small amount of the α isomer, is formed.

From the more detailed conversion plots in Figure 8c,d it can be seen that the α isomer represents a considerable part of the initial product distribution in the beginning of the reaction. However, after a short initialization period, the β(E) isomer is formed (almost) exclusively, which might be attributed to, for example, conformational changes, steric effects, or coordinative...
influences of the alkylic products. When the catalyst was used without additives and a proton source was added after 90 minutes, the total amount of β and β(2) isomers did not change, which shows that the change in product distribution upon protonation can indeed be attributed to a different selectivity and not to isomerization processes. By contrast, oxidation leads to a strong increase of the conversion rate upon protonation can indeed be attributed to a different change, which shows that the change in product distribution over the course of the reaction. However, the distribution of the α and β(2) isomers immediately changed to the ratio observed at the end of the catalysis, which demonstrates that the two isomers are in a thermal equilibrium (Figure 8a/b). As a proof of concept, we were thus able to show that both triggers act orthogonally, that is, they influence either the rate of conversion and/or the product distribution.

Overall, we report the synthesis of a novel type of redox-active and proton-sensitive phosphine ligand in which the donating capabilities can be switched orthogonally and reversibly by either protonation or oxidation. Structures of all ligands and their complexes were investigated by X-ray diffractions and NMR spectroscopy. The influence of protonation and coordination of a metal fragment on the redox behaviour was investigated by cyclic voltammetry, showing the sensitivity of the ferrocene moiety towards changes in the ligand system. Generally speaking, switching ligand properties in situ can greatly influence the reactivity and the selectivity of coordinated metals in catalysis. As a proof of concept, the rhodium(l) complex 3 reported in this study was applied as precatalyst in hydrosilylation reactions of 1-hexyne. When the different switches were applied, they influenced either the rate of conversion and/or the product distribution. We believe that this case study demonstrates that such orthogonally multiresponsive ligands allow for fine tuning of catalytic systems, and improve control in multimetallic catalysis. Further investigations in this area are currently being performed in our group.

Table 4. Conversion and product distribution of the catalytic hydrosilylation of hex-1-yne with triethyl silane at room temperature. Catalyst loading (3): 1 mol%.

| Additive[9] | t [min] | Conversion[9] (%) | β(2) : α(2) |
|------------|--------|-------------------|-------------|
| none       | 480    | 65                | 70:20:10    |
| [H(1,1-DOT)(CF3)2]3Al | 480    | 64                | 92: < 1:7   |
| [CpFe(C5H4Me)][SiF6]2 | 240    | 83                | 45: < 1:55  |

[a] Additive loading of 1 mol%. [b] Conversion and yields were determined by 1H NMR spectroscopy by integrating against (SiMe3)2O as internal standard. [c] The isomers were identified from their respective coupling constants.

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Conflict of Interest

The authors declare no conflict of interest.

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[1] a) O. R. Luca, R. H. Crabtree, Chem. Soc. Rev. 2013, 42, 1440–1459; b) V. Lyasovskyky, B. de Bruin, ACS Catal. 2012, 2, 270–279; c) L. A. Berber, B. de Bruin, A. F. Heyduk, Chem. Commun. 2015, 51, 1553–1556; d) V. Blanco, D. A. Leigh, V. Marcos, Chem. Soc. Rev. 2015, 44, 5341–5370; e) K. Arumugam, C. D. Varnado Jr., S. Spiroules, V. M. Lynch, C. W. Bielawski, Chem. Eur. J. 2013, 19, 10866–10875; f) J. Choudhury, Tetrahedron Lett. 2018, 59, 487–495; g) C. Ruiz-Zambrana, A. Gutiérrez-Blanco, S. Gonell, M. Poyatos, E. V. Peris, Angew. Chem. Int. Ed. 2021, 60, 20003–20011; Angew. Chem. 2021, 133, 20156–20164; h) P. Pandey, P. Daw, N. U. Din Reshi, K. R. Ehmnn, M. Hölscner, W. Leitner, J. K. Bera, Organometallics 2020, 39, 3849–3863; i) M. Kaur, N. U. Din Reshi, K. Patra, A. Bhattacharya, S. Kunikuruvan, J. K. Bera, Chem. Eur. J. 2021, 27, 10737–10748.
[2] a) J. Ang, A. L. Tolman, Chem. Rev. 1977, 77, 313–348; b) D. J. Nelson, S. P. Nolan, Chem. Soc. Rev. 2013, 42, 6723–6753.
[3] a) L. E. Rosen, C. D. Varnado, A. G. Tennyson, D. M. Khamrov, J. W. Kamplain, D. H. Sung, P. T. Cresswell, V. M. Lynch, C. W. Bielawski, Organometallics 2009, 28, 6695–6706.
[4] A. Feyrer, M. K. Armbruster, K. Fink, F. Breher, Chem. Eur. J. 2017, 23, 7402–7408.
[5] L. Hettmanczyk, L. Suntrup, S. Kleink, C. Hoyer, B. Sarkar, Chem. Eur. J. 2017, 23, 576–585.
[6] For further readings on redox switchable NHCs: Y. Ryu, G. Ahumada, C. W. Bielawski, Chem. Commun. 2019, 55, 4451–4466.
[7] a) M. Abubekeroev, V. Vlček, J. Wei, M. E. Miehlich, S. M. Quan, K. Meyer, D. Neuhausser, P. L. Diancosene, Science 2018, 7, 120–131; b) M. Abubekerov, S. M. Shepard, P. L. Diancosene, Eur. J. Inorg. Chem. 2016, 2634–2640; c) A. B. Biehnsen, K. R. Delle Chiaie, J. B. Curley, J. A. Byers, Angew. Chem. Int. Ed. 2016, 55, 5225–5230; Angew. Chem. 2016, 128, 5337–5340; d) E. M. Broderick, N. Guo, T. Wu, C. S. Vogel, C. Xu, J. Sutter, Angew. Chem. Int. Ed. 2015, 54, 9897–9899; e) L. A. Brown, J. L. Rivonheit, B. K. Long, Angew. Chem. 2015, 5, 6057–6060; f) R. Dai, P. L. Diancosene, Dalton Trans. 2019, 48, 2996–3002; g) C. K. A. Gregson, I. J. Blackmore, V. C. Vogel, C. Xu, J. Sutter, J. T. Miller, K. Meyer, T. Cantat, P. L. Diancosene, Chem. Commun. 2011, 47, 9987–9989; h) E. M. Broderick, N. Guo, T. Wu, C. S. Vogel, C. Xu, J. Sutter, J. T. Miller, K. Meyer, T. Cantat, P. L. Diancosene, Chem. Commun. 2011, 47, 9987–9989; i) L. A. Brown, J. L. Rivonheit, B. K. Long, Coord. Chem. Rev. 2018, 372, 141–152; j) A. Lai, Z. C. Hernandez, P. L. Diancosene, ChemCatChem 2019, 11, 4210–4218; k) M. Y. Lowe, S. Shu, S. M. Quan, P. L. Diancosene, Inorg. Chem. Front. 2017, 4, 1798–1805; l) M. Qi, Q. Dong, W. Wang, J. A. Byers, J. Am. Chem. Soc. 2018, 140, 5686–5690; m) S. M. Quan, X. Wang, R. Zhang, P. L. Diancosene, Macromolecules 2016, 49, 6768–6778; n) S. M. Quan, J. Wei, P. L. Diancosene, Organometallics 2017, 36, 4451–4457; o) X. Wang, A. Thevenon, J. L. Brosmer, I. Yu, S. I. Khan, P. Mehrkhodavandi, P. L. Diancosene, J. Am. Chem. Soc. 2014, 136, 11264–11267; p) J. Wei, P. L. Diancosene, Acc. Chem. Res. 2019, 52, 413–424; q) J. Wei, M. N. Riffel, P. L. Diancosene, Macromolecules 2017, 50, 1847–1869.
[8] E. M. Broderick, N. Guo, C. S. Vogel, C. Xu, J. Sutter, J. T. Miller, K. Meyer, P. Mehrkhodavandi, P. L. Diancosene, J. Am. Chem. Soc. 2011, 133, 9278–9281.
[9] a) Y. Shen, S. M. Shepard, C. J. Reed, P. L. Diaconescu, Chem. Commun. 2019, 55, 5587–5590; b) S. Ibáñez, M. Poyatos, L. N. Dawe, D. Gusev, E. Peris, Organometallics 2016, 35, 2747–2758.
[10] a) E. Deck, H. E. Wagner, J. Paradies, F. Breher, Chem. Commun. 2019, 55, 5323–5326; b) A. Feyrer, F. Breher, Inorg. Chem. Front. 2017, 4, 1125–1134.
[11] I. M. Lorkovic, R. R. Duff, M. S. Wrighton, J. Am. Chem. Soc. 1995, 117, 3617–3618.
[12] a) E. Deck, H. E. Wagner, J. Paradies, F. Breher, Chem. Commun. 2019, 55, 5323–5326; b) A. Feyrer, F. Breher, Inorg. Chem. Front. 2017, 4, 1125–1134.
[13] P. Mehlmann, F. Dielmann, Chem. Eur. J. 2019, 25, 2352–2357.
[14] B. M. Neilson, V. M. Lynch, C. W. Bielawski, Angew. Chem. Int. Ed. 2011, 50, 10322–10326; Angew. Chem. 2011, 119, 10506–10510.
[15] a) S. Galkwad, A. Goswami, S. De, M. Schmittel, Angew. Chem. Int. Ed. 2016, 55, 10512–10517; Angew. Chem. 2016, 128, 10668–10673; b) J. Choudhury, S. Semwal, Synlett 2018, 29, 141–147.
[16] R. H. Crabtree, New J. Chem. 2011, 35, 18–23.
[17] M. Neel, P. Retailleau, A. Voituriez, A. Marinetti, Organometallics 2018, 37, 797–801.
[18] Recent reviews on sandwich compounds: a) D. E. Herbert, U. F. J. Mayer, I. Manners, Angew. Chem. Int. Ed. 2007, 46, 5060–5081; Angew. Chem. 2008, 119, 5152–5173; b) M. Tamm, Chem. Commun. 2008, 3089–3100; c) H. Braunschweig, T. Kupfer, Acc. Chem. Res. 2010, 43, 455–465; d) H. Bhattacharjee, J. Müller, Coord. Chem. Rev. 2016, 314, 114–133.
[19] a) A. N. Nesmejanow, W. A. Ssasonowa, V. N. Drosd, Chem. Ber. 1960, 93, 2717–2729; b) M. Herberhold, H.-D. Brendel, J. Organomet. Chem. 1993, 458, 205–209; c) I. Noviandri, K. N. Brown, D. S. Fleming, P. T. Gulyas, P. A. Lay, A. F. Masters, L. Phillips, J. Phys. Chem. B. 1999, 103, 6713–6722.
[20] a) P. Zanello, Inorganic Electrochemistry: Theory, Practice and Application, RSC, Cambridge, 2003; b) B. Neumann, U. Siemeling, H.-G. Stammier, U. Vorfeld, J. G. P. Delis, P. W. N. M. van Leeuwen, K. Vrieze, J. Fraanje, K. Goubitz, F. Fabrizi de Biani, J. Chem. Soc. Dalton Trans. 1997, 4705–4712.
[21] R. Mäty, B. S. Birenheide, F. Breher, B. Sarkar, ChemCatChem 2021, 13, 2337–2370.
[22] Deposition Numbers 2087629 (for L1), 2087627 (for L2), 2087630 (for 1), 2087635 (for 2), 2087632 (for 4), 2087636 (for 5), 2087631 (for 6), 2087633 (for L1H+), 2087634 (for 2H+) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.