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Synthetic Methods

Organic Transformations on σ-Aryl Organometallic Complexes

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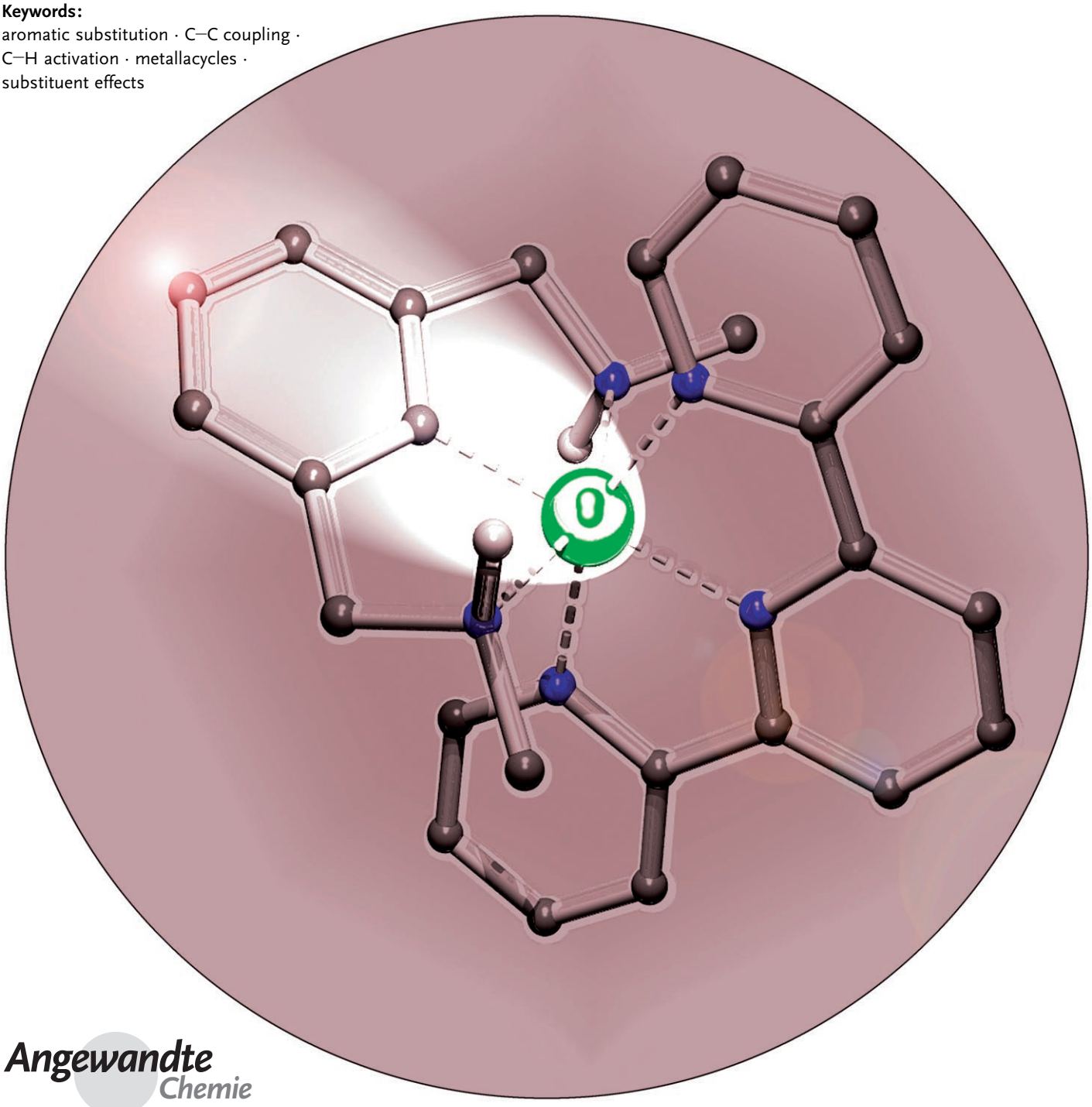
aromatic substitution · C–C coupling · C–H activation · metallacycles · substituent effects



This work reviews recent developments in the field of organic transformations on σ-aryl organometallic complexes. The general notion that M–C σ bonds are kinetically labile, highly reactive, and incompatible with typical reaction conditions met in organic synthesis has limited the use of these synthetic strategies thus far. However, organic transformations on metal-bound σ-aryl fragments are being used more and more by chemists in both industry and academia. In this Review, emphasis is put on the synthetic methods applied in this field up to now. The simplicity and generally good yields of these methods are very attractive for the construction of functionalized organometallic building blocks that are potentially useful as photochemical molecular devices, biosensors and -conjugates, or molecular switches. Thus, this Review has been tailored for a broader audience with the aim of encouraging the application of these strategies.

From the Contents

1. Introduction

The use of organometallic complexes in chemo-, regio-, and stereoselective catalytic and stoichiometric reactions between organic substrates has increased tremendously in the last 50 years. In the early days, organometallic derivatives containing Li, Mg, Zn, or Sn were merely employed as intermediates for subsequent stoichiometric organic reactions. Their use provided numerous strategies for efficient C–C bond-formation reactions with functionalized molecules. In the early 1950s, the significant growth of the field of organometallic chemistry with transition metals started.[1] The discovery of ferrocene[2] and subsequent seminal work by Wilkinson et al.,[3] Fischer,[4] and Chatt[5] provided a basis for the fundamental understanding of the factors that govern the stability and structure of well-defined transition-metal organometallic complexes.[6] By 1980, organometallic chemistry became an important subdiscipline of inorganic and coordination chemistry. The importance of (organo)transition-metal-based catalytic processes for the production of bulk chemicals and polymers initiated an immense amount of research in academia and industry. Studies focussed on the kinetic[7] and thermodynamic[8] factors involving M–C bond formation and cleavage and thus on the mechanistic aspects of economically viable processes.

In recent years, organometallic chemistry has been in the midst of a transition to a much broader and more interdisciplinary role.[9] The rules to fine-tune and control the electronic and/or steric effects in complexed transition-metal centers allow the application of organometallic complexes in diverse areas of molecular sciences. For example, they can be used in homogeneous and heterogeneous catalytic systems[10] as well as functional units in polymers[11] and dendrimers,[12] as gas-sensing devices,[13] biomarkers[14] or electro-optical devices,[15] and as liquid-crystalline materials.[16] In general, two strategies for the preparation of organometallic complexes containing σ-bound aryl groups can be applied. The first involves the multistep preparation of a ligand with one or more of the desired metal-binding domains which can be subsequently metalated.[17] In this synthetic protocol the introduction of the transition-metal center(s) in the organic ligand is typically the last step. This order seems logical because the $M–C_{ipso}$ σ bond is often regarded as the most reactive and sensitive part of the organometallic structure. Drawbacks of this strategy are the sometimes long and complex synthesis of the ligands and the frequently incomplete metalations, which lead to tedious separation procedures of unreacted ligands and metal residues. The second strategy involves the preparation of organometallic building blocks bearing suitable functionalities. This latter strategy can be used to modify the ligand sphere around the metal center without elaborate synthesis and has been explored with success for π-aryl organometallic systems such as ferrocene and its derivatives.[18] However, functionalization of σ-aryl organometallic complexes remained relatively unexplored owing to the low stability often associated with these compounds. In fact, common practice has shown that the M–C σ bond is usually cleaved by highly reactive reagents. Also, the presumption that compounds with a σ-aryl (or σ-alkyl) metal bond would be too reactive to survive direct modification of the ligand sphere hampered further application. Furthermore, exchange or decomplexation of kinetically labile ligands was found to be responsible for the formation of side products or the breaking of M–C bonds during the functionalization of σ-aryl complexes.

In the 80s and 90s, van Koten et al.,[19a] and Roper et al.[20] demonstrated that σ-aryl complexes of late transition metals such as platinum(II), ruthenium(II), and osmium(II) are sufficiently inert and can undergo a wide range of organic

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transformations on the ligands. Of the several ligand systems successfully applied cyclometalated complexes proved to be superior in protecting the M–C σ bond towards degradation under the employed reaction conditions. It was shown that several advantages are offered by this synthetic approach: 1) The preparation of a specifically substituted aryl ligand is not required, 2) functionalization of the aryl–metal complexes can be achieved without using tin, lithium, and mercury transmetalation agents, and 3) the application of oxidative addition of an aryl–halide bond to low-valent metal centers is not necessary.[21] Moreover, a single metalation step is involved, and difficulties such as incomplete metalation are circumvented. The presence of a transition metal can have other beneficial advantages for functionalization of the organic ligand. When the ligand is not coordinated to the metal center, functionalization may not occur selectively and mixtures of products are obtained. In contrast, the metal atom itself can exert mesomeric and inductive effects on subsequent substitution processes on the σ-bonded aryl ring.

The main purpose of this review is to describe typical organic transformations on σ-type organometallic complexes. In general, only two different classes of reactions are encountered: 1) electrophilic substitution of aryl rings in organometallic complexes and 2) metal-mediated cross-coupling reactions of these aryl ligands to generate C–C bonds while retaining the M–C σ bond. The first topic highlights cases in which functionalization of σ-aryl organometallic units was achieved, with special attention to activating and directing effects of the metal center on the substitution process. The second topic is of more recent interest and concerns the functionalization of cyclometalated complexes by chemical transformations, that is, cross-coupling reactions, leading to the incorporation of the cyclometalated building blocks in more sophisticated architectures such as molecular wires and switches. It also must be pointed out that, although in its infancy, recent studies showed that subsequent removal of the metal from the newly substituted organometallic compounds could constitute a novel route to unusually substituted ligands, that is, organic products which would otherwise be difficult to prepare by the more general synthetic routes. In this case, the metal-complex fragment can be considered to act as a "protecting group" which also directs the substitution process at the σ-bonded aryl ring.

2. Regioselective Electrophilic Substitution of σ-Bonded Aryl Groups

In 1994, Roper and co-workers reported the first example of a direct nitration of aryl groups σ-bonded to Ru^{II} as a method to prepare nitroaryl-containing ruthenium complexes without affecting the M–C bond.[20] A well-known procedure for the nitration of reactive and acid-sensitive arenes involves the use of copper(II) nitrate in the presence of acetic anhydride (Menke conditions;[22] Scheme 1).

At that time, syntheses of nitroaryl-containing organometallic complexes were performed by transmetalation,[17c,21] direct reaction of a nitroaryl compound with metal halides,[23]

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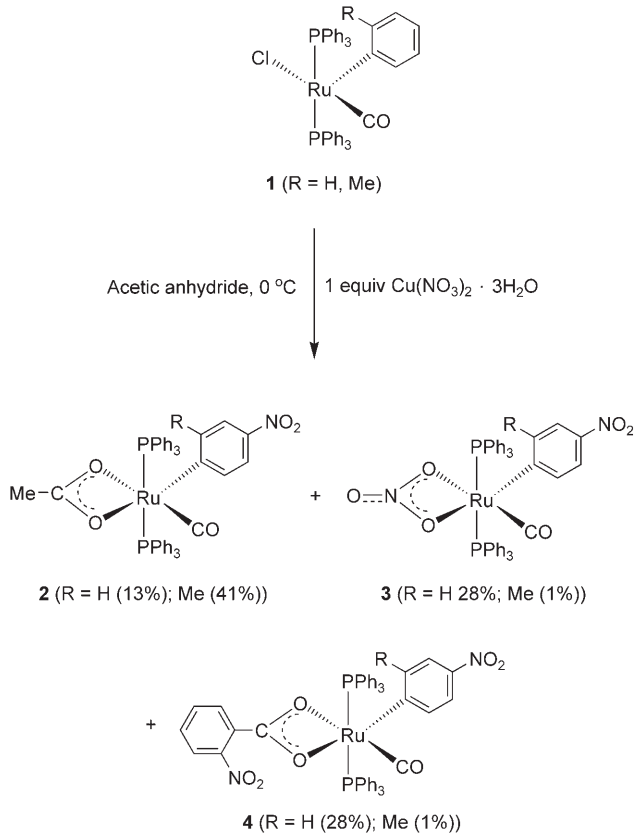
Preston Chase was born in 1975 in Victoria, Canada. In 1998, he obtained a B.Sc. in Chemistry from the University of Victoria and, in 2003, a PhD from the University of Calgary on highly fluorinated 9-borafluorene Lewis acids with Warren Piers. He then joined the group of Prof. van Koten at Utrecht University as an NSERC postdoctoral fellow researching new methods in pincer-templated macrocycle synthesis. He is currently with Doug Stephan at the University of Windsor (Canada) developing metal-free hydrogenation catalysts.

Dennis J. M. Snelders was born in 1981 in Goirle, The Netherlands and studied chemistry at Utrecht University, where he received his M.Sc. degree in 2004. After an internship in industry with Organon, Oss, he returned to Utrecht University in 2005, where he started working on his PhD thesis under the supervision of Prof. G. van Koten and Prof. Klein Gebbink. He investigates the application of polycationic dendritic phosphines in homogeneous catalysis.

Bert Klein Gebbink, born 1969 in Lichtenvoorde, The Netherlands, obtained his PhD in 1998 from Nijmegen University with Prof. R. J. M. Nolte in the field of supramolecular and bioinorganic chemistry. After a postdoctoral stay at Stanford University in the group of Prof. T. D. P. Stack, he joined the group of Prof. van Koten at Utrecht University in 1999 as a postdoctoral fellow. In 2002 he was appointed assistant professor and later in 2005 associate professor in the van Koten group. In 2006 he was promoted to full professor at Utrecht University. His current research interests include homogeneous catalysis, bioinorganic chemistry, and metals in chemical biology.



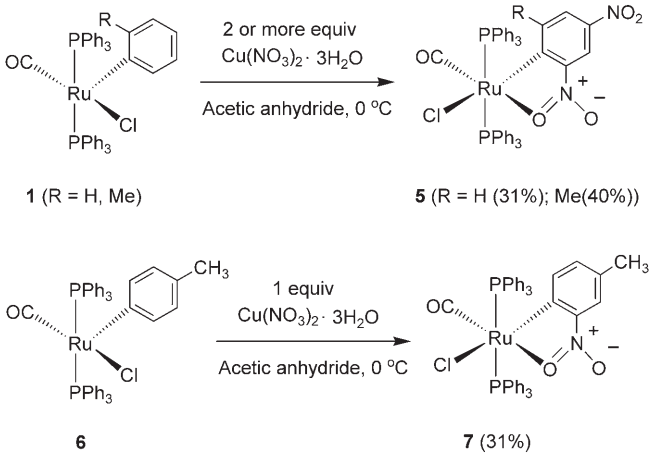
Scheme 1.

Gerard van Klink obtained his PhD from the Vrije Universiteit, Amsterdam, with Prof. F. Bickelhaupt on the mechanism of formation of organomagnesium compounds. He worked as a postdoctoral fellow in the group of Prof. J. J. Eisch at the State University of New York at Binghamton, in cooperation with DSM Research. From 1998 until 2007 he worked as a lecturer in the group of Prof. van Koten. His research interests comprise the study of fundamental organic synthetic processes, the use of combinatorial and computational methods in organometallic chemistry, the application of organometallic complexes as catalysts and as materials with special physicochemical properties.

Gerard van Koten has been Professor of Organic Chemistry and Catalysis at Utrecht University since 1986 and became Distinguished Professor of Utrecht University in 2004. Since 2005 he has acted as Dean of the Faculty of Science at Utrecht University. His research interests comprise the study of fundamental processes in organometallic chemistry and the application of organometallic complexes as homogeneous catalysts. His interest in supramolecular systems with (organometallic) catalytically active functionalities include the preparation and use of the first examples of homogeneous metallodendrimer catalysts.

oxidative addition of nitroaryl halides to low-valent transition-metal centers,[21a] and the reaction of 4-nitrophenylhydrazine with a metal halide.[24] As shown in Scheme 1, the presence of a σ-bonded Ru^{II} center in complex **1** induces a strong *para*-directing effect, resulting in exclusive nitration of the 4-position in the aryl ring in all cases. However, this new procedure led to the formation of a mixture of products, probably arising from aryl–ligand exchange during the course of the reaction (Scheme 1). $[RuCl_3(NO)(PPh_3)_2]$ and other unidentified nitrosyl-containing complexes were also present as impurities in the crude samples, but their removal could be effected by fractional crystallization or by column chromatography. The origin of the 2-nitrobenzoate ligand in **4** is uncertain. Its formation possibly occurs through a radical reaction during the nitration process. Notably, **3** and **4** may be converted back into **2** by recrystallization in the presence of an excess of sodium acetate.

The ruthenium center also exerts an *ortho*-directing effect, as illustrated by the fact that dinitrated complex **5** (Scheme 2) can be prepared when two or more equivalents of

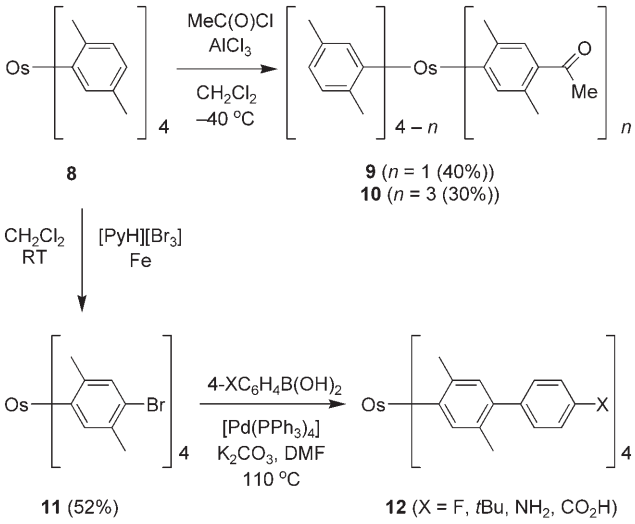


Scheme 2.

copper(II) nitrate are used. It must be noted that the *para*- and *ortho*-directing effect of the ruthenium center in the aryl group apparently is stronger than that of the methyl group. In fact, nitration of toluene under similar experimental conditions (HNO_3, acetic anhydride, 30 °C) yields 58.4% of *o*-nitrotoluene, 4.4% of *m*-nitrotoluene, and 37.2% of *p*-nitrotoluene. Despite the normally deactivating influence of the nitro group in an aromatic ring for further electrophilic substitution, introduction of a second nitro group to a nitroaryl ligand σ-bonded to a ruthenium center appeared to be extremely facile. The reason for this observation is probably a combination of two factors: the activating influence of the ruthenium center on the electrophilic substitution process and the formation of an energetically stable metallacycle. The *ortho*-chelating interaction between an *ortho*-NO_2 group and the metal center has been observed in other *o*-nitroderivatives. However, when the preferred *para* position is blocked by substitution (**6**, Scheme 2), the aryl ring is exclusively nitrated at the *ortho* position relative to the Ru–C bond, leading to the formation of **7**.

Roper and co-workers showed that the 4-nitrophenyl ligand in the prepared complexes can be reduced with zinc and hydrochloric acid to produce 4-aminoaryl ruthenium complexes. The latter complex could be acetylated to the corresponding amide,[25] again highlighting the stability of the Ru–C_{aryl} σ bond.

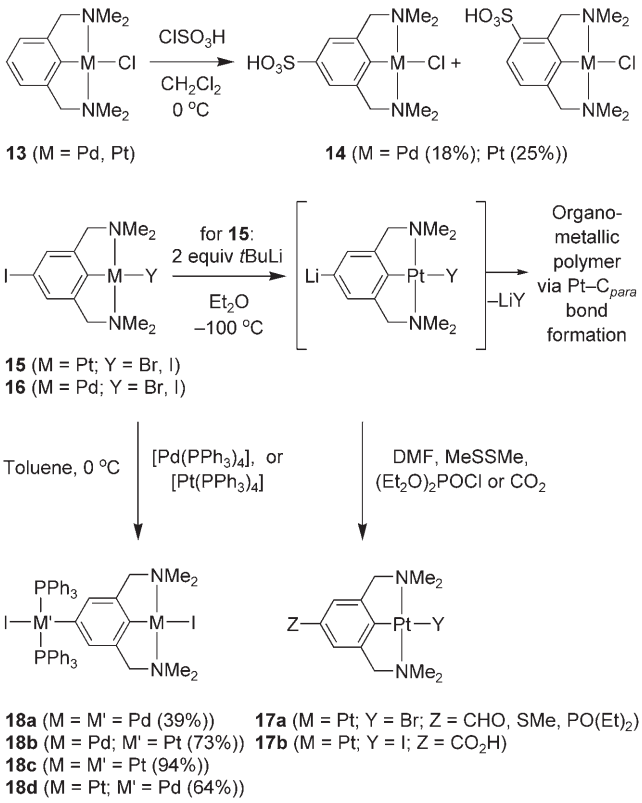
Functionalization of the aryl group in Os^{IV}–tetraaryl complexes by electrophilic attack (e.g. bromination or acylation) without cleavage of the Os–C_{aryl} σ bond has been reported by Lau et al.[26] Regioselective bromination of the *para* positions on each of the four 2,5-dimethylphenyl ligands of complex **8** (Scheme 3) has been carried out by reaction



Scheme 3.

with pyridinium tribromide in the presence of a catalytic amount of iron powder. The resultant homoleptic tetrakis-(bromoaryl)osmium compound **11**, which can be used to synthesize organometallic oligomers/polymers, has proven to be a good starting material for metal-catalyzed cross-coupling reactions.[26] It undergoes Suzuki coupling with 4-$XC_6H_4B(OH)_2$ (X = F, *t*Bu, NH_2, CO_2H) in the presence of $[Pd(PPh_3)_4]$ to afford the respective osmium complexes **12**. The electron-rich σ-aryl groups in **8** are also prone to Friedel–Crafts acylation. Treatment of **8** with MeC(O)Cl in the presence of $AlCl_3$ affords a mixture of complexes in which either one (**9**) or three (**10**) ligands are substituted with an acetyl group, again at the *para* position. Remarkably, no bis- or tetrakis-substituted acetyl–aryl products were observed.

Van Koten and co-workers demonstrated that Pd^{II} and Pt^{II} complexes of the monoanionic, terdentate coordinating NCN pincer ligand 2,6-bis[(dimethylamino)methyl]phenyl (**13**, Scheme 4; NCN = $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$) undergo regioselective electrophilic substitution. The crude product obtained by treating **13** with chlorosulfonic acid in CH_2Cl_2 contained the *para*-metalated arylsulfonic acids **14** (ca. 50%) together with an amount of the *meta* isomer (ca. 30%) and unidentified decomposition products.[27] Purification of **14** could be achieved by precipitation from the reaction mixture with MeCN or MeOH. However, separation of the *para* isomers **14**



Scheme 4.

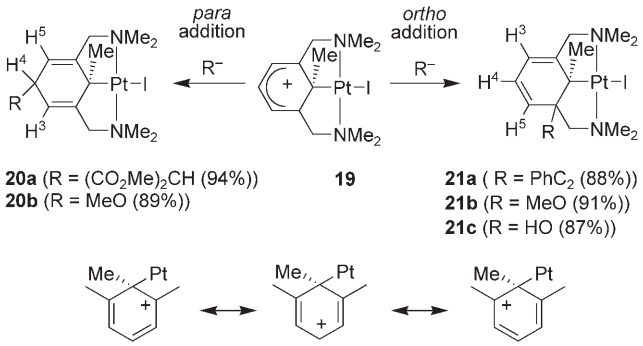
from the *meta* isomers proved to be difficult and caused a considerable loss of material. Thus, analytically pure **14** was obtained only in low yield.

The *para*-iodo-substituted NCN–Pt^{II} pincer complex **15** proved to be a convenient starting material for further modifications.[28] Remarkably, **15** can be lithiated using *t*BuLi without disruption of the Pt–C bond and without transmetalation with the Pt–Cl group. The resulting organolithium compounds were treated in situ with different nucleophiles to give in good to excellent yields, after hydrolysis, *para*-substituted complexes of type **17**. The high stability of **17b** in aqueous and aerobic media allowed its application for the synthesis of bio-organometallic species in which the complex was anchored to the N and C terminus and the α-carbon atom of different amino acids as well as carbohydrates.[29] Attempts to lithiate the corresponding *para*-iodo NCN–Pd^{II} pincer complex **16** resulted in decomposition and did not allow the exploration of these unconventional strategies for *para* functionalization of the corresponding palladium complexes.

Thus, *para*-fuctionalized NCN–Pd^{II} pincer complexes had to be prepared by metalation of prefunctionalized *para*-substituted NCN pincer ligands. Oxidative addition of the C–I bond in **15** and **16** to $[Pd(PPh_3)_4]$ or $[Pt(PPh_3)_4]$ gave the bimetallic complexes **18**.[28] Interestingly, **18a** reacted regioselectively with 1-alkynyl derivatives (Sonogashira-like reaction) exclusively through the non-cyclometalated palladium center.[28]

Although not belonging to the class of reactions described here, it is worthwhile to mention the functionalization of the cationic complex $[PtI\{MeC_6H_3(CH_2NMe_2)_2\text{-}2,6\}]BF_4$ (**19**,

Scheme 5) reported by van Koten and co-workers.[19] In fact, the reactivity shown by **19** can be seen as a direct counterpart to electrophilic aromatic substitution reactions of metal-



20a (R = $(CO_2Me)_2CH$ (94%))
20b (R = MeO (89%))

19

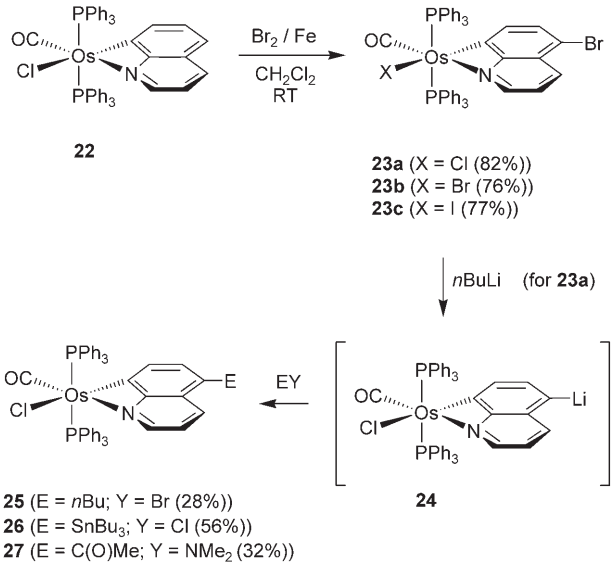
21a (R = PhC_2 (88%))
21b (R = MeO (91%))
21c (R = HO (87%))

Scheme 5.

substituted benzene rings. At low temperatures and in appropriate solvents, the arenium complex **19** is susceptible to attack by nucleophilic reagents (e.g. $CH(CO_2Me_2)_2^-$, $PhC{\equiv}C^-$, MeO^-, HO^-) on the C_6H_3 ring at either the *ortho* or *para* positions with respect to the Pt–C σ bond. This attack leads to the selective formation of localized C–C or C–O bonds, that is, formation of either 2,5- or 2,4-cyclohexadiene systems. The platinum center in these compounds retains its formal oxidation state of +2 with a square-planar geometry in which the *ortho*-Me_2NCH_2 ligands remain *trans*-coordinated. Calculations on model arenium compounds pointed to the presence of a positive charge density at both *ortho* and *para* positions.[19b] This charge, as a natural consequence of the mesomeric structures depicted in Scheme 5, explains the activation of these positions towards regiospecific nucleophilic addition. The possibility of performing both electrophilic aromatic substitution and subsequent nucleophilic addition reactions on the NCN pincer complexes with d^8 metals proved the versatility of these systems, in which the M–C σ-bond is retained. Importantly, decomposition of the products owing to either protonation of the amine donor arms of the NCN pincer ligand, or to hydrolysis of the Pt–C σ bond, does not occur despite the presence of strong acids in the workup of the reaction mixtures.

3. Regioselective Electrophilic Substitution of Heterocyclic Polyaromatic Ligands

The results discussed in the previous section prompted Roper et al. to extend their research towards the functionalization of σ-aryl organometallic complexes containing various aromatic heterocyclic ligand systems. Regioselective bromination of the quinolyl ligand in Os^{II} complex **22**, which was carried out at room temperature in dichloromethane with one equivalent of bromine and a catalytic amount of iron powder, was reported (Scheme 6).[30] The activating *ortho*/*para*-directing effect of the osmium center facilitates electrophilic aromatic substitution at the 5-position under mild conditions. Under the applied reaction conditions also some **23b**, in



22

23a (X = Cl (82%))
23b (X = Br (76%))
23c (X = I (77%))

25 (E = *n*Bu; Y = Br (28%))
26 (E = $SnBu_3$; Y = Cl (56%))
27 (E = C(O)Me; Y = NMe_2 (32%))

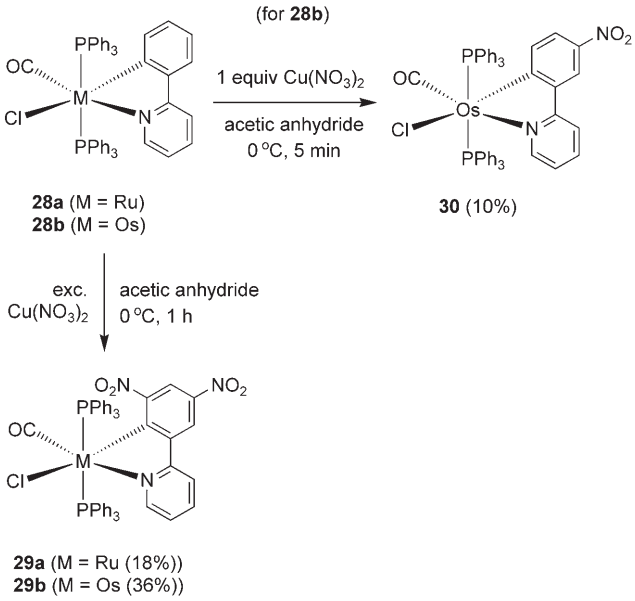
24

Scheme 6.

which the chloride ligand is replaced by bromide, was formed. This halide scrambling at the Os center was overcome by treatment of the reaction mixture with $AgBF_4$ and subsequent addition of the appropriate sodium halide.

The selective and mild bromination of the quinolyl ligand under these conditions is remarkable as free quinoline undergoes classical bromination only under forcing conditions with the formation of a mixture of products.[31] Interestingly, bromination of nonchelated naphthyl derivatives $[OsCl(1\text{-naphthyl})(CO)(PPh_3)_2]$ under the same reaction conditions resulted in cleavage of the Os–naphthyl bond. This result highlights again the key role played by chelation to stabilize the M–C σ bond. The robust four-membered chelate ring in **23a**, in which the 8-quinolyl ligand is bound through C8 and the N atom, persists during many chemical transformations. Treatment of **23a** with *n*BuLi gave intermediate **24**, which underwent further reactions typical of aryllithium reagents (Scheme 6).[30] This constitutes a valuable route to the introduction of a wide range of functional groups (see complexes **25**–**27**).

Electrophilic substitution of a 2-phenylpyridine ligand was also investigated.[32] Nitration of free 2-phenylpyridine itself, performed by heating 2-phenylpyridine with HNO_3 in concentrated H_2SO_4 at 100 °C for 30 min,[33] occurred at the phenyl ring to give two mononitrated isomers, the major product being that with the nitro group *para* to the C–C σ bond. However, the ruthenium or osmium-bonded ligand is highly activated towards nitration at both the *para* and the *ortho* position. Stirring complexes **28** for 1 h at room temperature with an excess of copper(II) nitrate in acetic anhydride gave exclusively dinitrated **29** (Scheme 7). Clearly, introduction of the first nitro group does not deactivate the phenyl ring toward further nitration. However, ruthenium complex **29a** is obtained in very low yield (18%), even when the reaction is performed at 0 °C. The *para*-substituted mononitrated osmium complex **30** was prepared when **28b** was treated with one equivalent of $Cu(NO_3)_2$ only for 5 min under similar

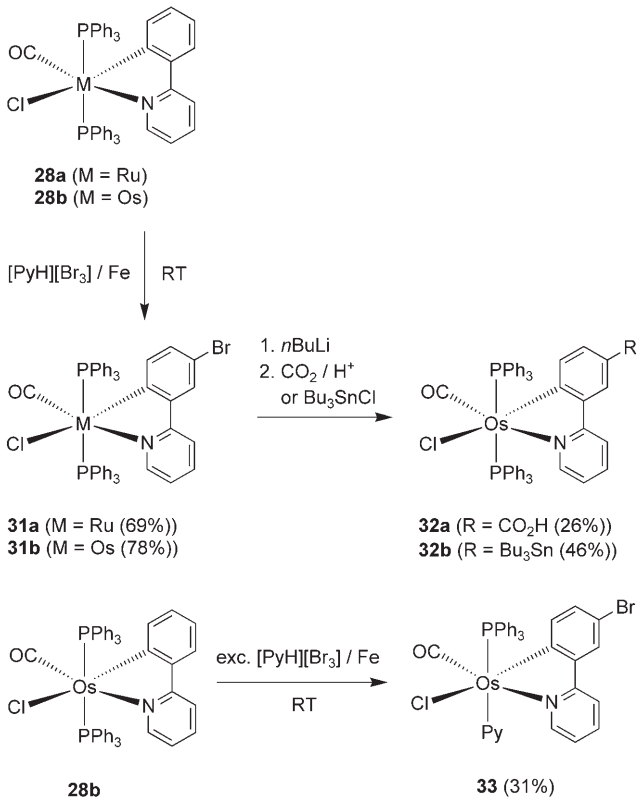


Scheme 7.

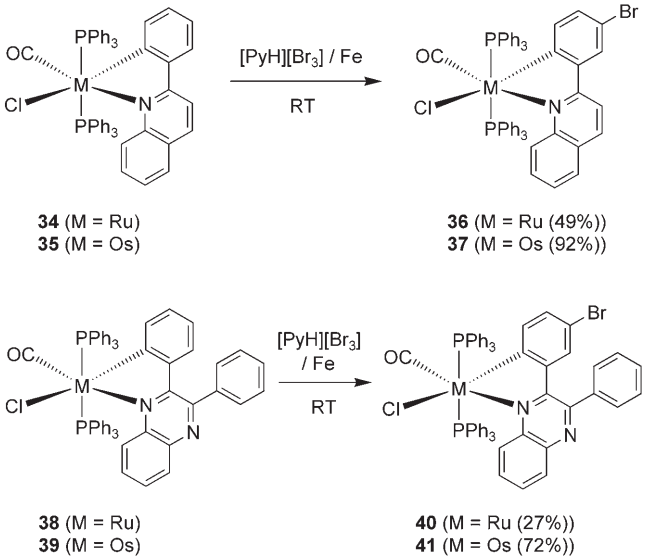
nitrating conditions.[32] Attempts to mononitrate the *para* position of the corresponding ruthenium complex **28a** failed. This result shows that subtle differences in the activating properties within one group of the periodic table exist.

Bromination of metal-bound 2-phenylpyridine in **28** with $[PyH][Br_3]$ in the presence of catalytic amounts of iron powder led to results analogous to the quinolyl system **22** (see above). The reaction is highly selective and occurs exclusively at the 4-position of the phenyl ring (**31**, Scheme 8).[32] Unlike the nitration reaction, no dibrominated products are formed, even when an excess of $[PyH][Br_3]$ or longer reaction times are used. Under these conditions, pyridine molecules oxidized by the excess of bromine can replace one of the PPh_3 ligand in complex **31b**, leading to the selective formation of **33**. Further functionalization of the brominated osmium complex **31b** may be conveniently achieved by lithiation and subsequent treatment with CO_2/H^+, yielding carboxylic acid derivative **32a**. Similarly, treatment of the lithiated intermediate with Bu_3SnCl gives the stannylate complex **32b**.[32]

More recently, cyclometalated multiaromatic heterocyclic ligands such as 2-phenylquinoline or 2,3-diphenylquinoxaline C,N-coordinated to ruthenium and osmium were subjected to electrophilic substitution reactions such as bromination and nitration.[34] Again, it is interesting to point out that under the mild reaction conditions the nonmetalated ligands are not activated towards functionalization. Bromination of the σ-bond aryl ring in these air-stable ruthenium and osmium species **34**, **35**, **38**, and **39** was carried out at room temperature by using one equivalent of $[PyrH][Br_3]$ together with a catalytic amount of iron powder (Scheme 9). Similarly to the systems discussed previously, a bromo substituent was introduced selectively at the 4-position of the phenyl ring, *para* to the M–C σ bond. No differences in reactivity of the ruthenium and osmium complexes were observed in this case, and products in which substitution occurred at the *ortho* position relative to the M–C σ bond were formed in low yield.

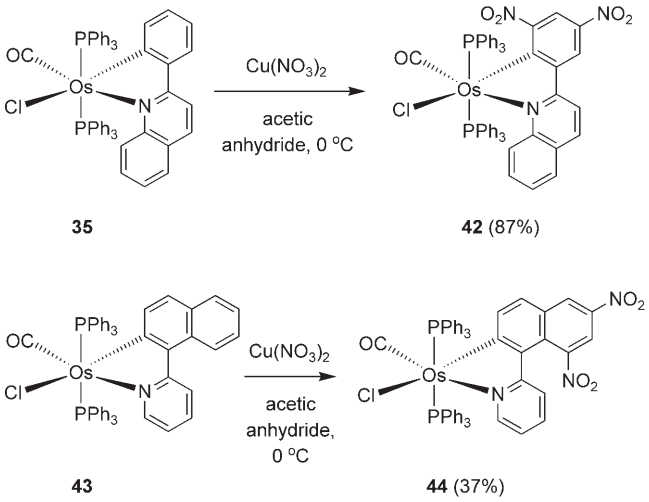


Scheme 8.



Scheme 9.

For nitration, carried out in a slurry of copper(II) nitrate in acetic anhydride, only the osmium complexes **35** and **43** were tested (Scheme 10). However, unlike the analogous compounds containing the smaller phenylpyridine and 8-quinolyl ligands, the nitrated products are formed more selectively and in higher yields.[34] For the 2-phenylquinoline system **35** the usual substitution pattern was observed; dinitrated complex **42** was obtained and both the *para* and

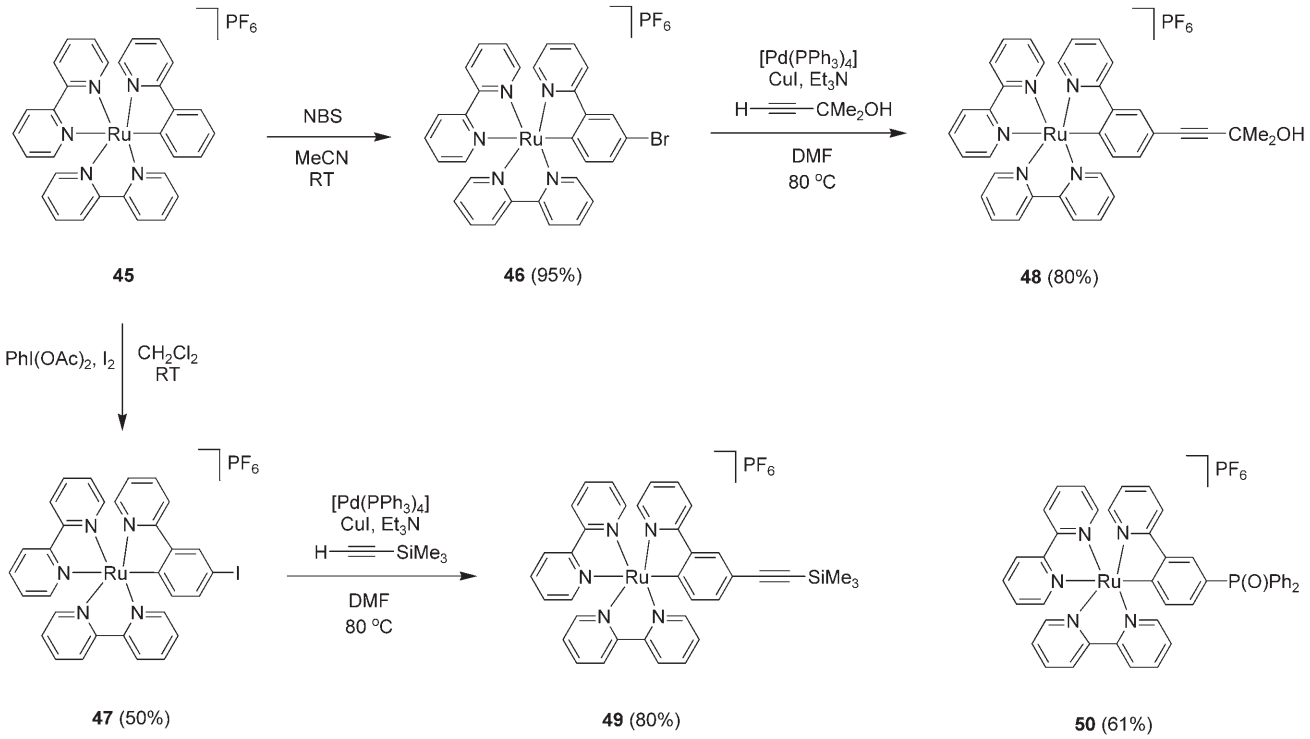


Scheme 10.

ortho positions relative to the metal center are activated. The outcome of the reaction of the 2-(1′-naphthyl)pyridine ligand in **43** differs significantly from other ligands (Scheme 10). In fact, the most activated and available site for substitution, the *para* position relative to the metal center, is an aromatic ring junction, rendering this position unavailable for functionalization. However, it was found that the 6- and the 8-positions in **43** are activated towards nitration, indicating that the electronic influence of the metal can be transmitted through the naphthyl ring via the conjugated π system.

Currently, a significant amount of research is being performed on the direct derivatization of mononuclear, cyclometalated Ru^{II} and Ir^{III} complexes. These compounds have potential in the construction of photochemical molecular devices (e.g. in solar energy conversion, electroluminescence, and information storage) because of their optical properties, which can be finely tuned. Furthermore, photoinduced energy- and electron-transfer processes in such complexes are currently being studied in great detail.[35] In the search for alternative and more efficient synthetic routes to these interesting synthons, Coudret et al.[36] investigated the regioselective functionalization of ruthenium(II) complex **45**, which contains both 2,2′-bipyridine and 2-phenylpyridine ligands (Scheme 11). These synthetic pathways constitute advantageous and efficient routes toward the construction of a great variety of polynuclear complexes through selective functionalization of one of the ring systems in the complex. Thus, treatment of **45** with *N*-bromosuccinimide (NBS) regioselectively afforded the *para*-brominated complex **46**. The fact that substitution only occurs at the phenyl ring of the phenylpyridine, rather than on the pyridine rings, clearly indicates that the activating effect of the ruthenium atom is transmitted more effectively through the M–C σ bond as compared to the M–N bond, in accord with the above studies.

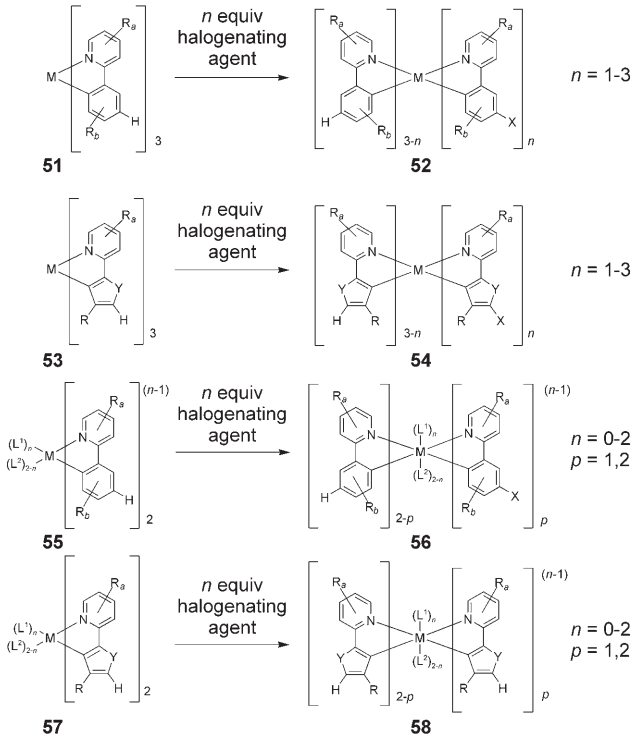
An attempt to prepare the iodo analogue **47** with *N*-iodosuccinimide resulted in degradation of the metal complex. However, degradation could be circumvented by using $PhI(OAc)_2/I_2$ as the iodinating agent.[36] Both **46** and **47** have been further employed as building blocks in metal-catalyzed coupling reactions. For example, through a Sonogashira alkynylation[37] ($[Pd(PPh_3)_4]$, CuI, Et_3N, DMF), both **46** and **47** reacted with the protected acetylenes 2-methylbut-3-yn-2-ol and trimethylsilylacetylene and gave the ruthenium(II) complexes **48** and **49** in good yield. A diruthenium(II)



Scheme 11.

complex could be prepared by reaction of **46** with the 9,10-bis-[(trimethylsilyl)ethynyl]anthracene spacer in a heterogeneous mixture of solid NaOH in DMF in the presence of aryl bromide and catalysts ($[Pd(PPh_3)_4]$ and CuI) at 80 °C. Interestingly, when the iodo complex **47** was subjected to the same procedure, no dinuclear complex was formed, but an efficient replacement of the I^- ligand for a $P(O)Ph_2$ group took place (**50**, 60 % yield; Scheme 11).[38]

The current upsurge in interest in organorhodium(III), and, in particular, organoiridium(III) complexes is justified not only by their interesting photo- and electroluminescent properties but also because of their superior capabilities to mediate photoinduced electron-transfer processes.[39] In this respect, the systematic work carried out by Stoessel and co-workers is of particular interest. This group showed that electrophilic aromatic substitution of the monometallic complexes **51**, **53**, **55**, and **57** (Scheme 12) is a versatile and



Scheme 12. M = Rh, Ir; X = F, Cl, Br, I; R = H, F, Cl, Br, NO_2, CN, alkyl, alkoxy, aryl, heterocyclic and polyaromatic groups; *a* = 0–4 (better yields with 0–2); *b* = 0–3 (better yields with 0, 1).

convenient methodology to directly functionalize (un)substituted heterocyclic multiaromatic ligands.[40] Regioselective halogenation was achieved in yields of 90–98 % with halogenating agents in the presence of a base. Owing to the activating and directing effect of the Rh^{III} or Ir^{III} centers, the aforementioned complexes underwent selective functionalization at the *para* position relative to the M–C σ bond. As the complexes bear three identical ligands, each having one position available for substitution, this reaction can yield mono-, di-, and trisubstituted products. Selectivity among these possibilities was elegantly achieved by simple stoichiometric control of the reaction.[40] When *n* equivalents (*n* = 1, 2, or 3) of halogenating agent are used, the product formed is selectively halogenated *n* times.

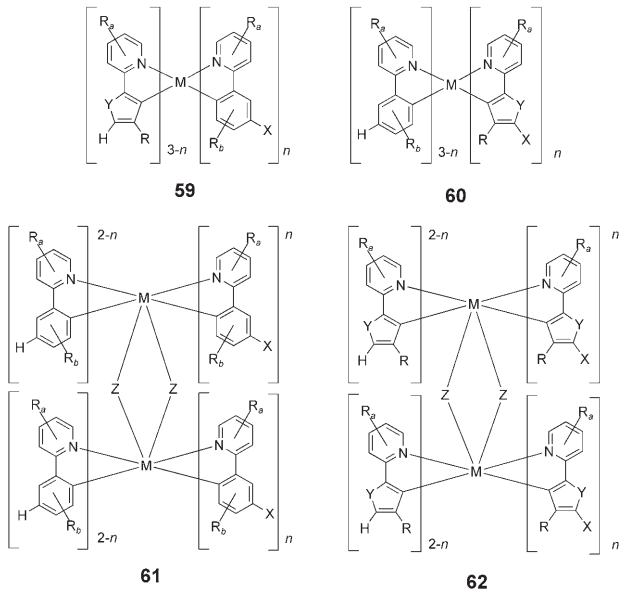
These results are surprising. In fact, it is expected that reaction of the unsubstituted complexes with one equivalent of halogenating agent results in a statistical mixture of products. These findings indicate that the monosubstituted products are by far less reactive than the unsubstituted ones. Although less activated, the mono- and disubstituted products can react further with a second or third equivalent of halogenating agent, yielding selectively the di- and trisubstituted products, respectively. If an excess from 3 to 1000 equivalents of halogenating agents is used, the trisubstituted product remains the only product obtained. However, when **51** and **53** are treated with an excess of nitrating agents, additional functionalization of the *ortho* position can occur as a side reaction.[41] These results are remarkable, but detailed investigations on the obtained selectivity have not been reported so far.

Many rhodium and iridium monomeric complexes were successfully subjected to this reaction. They differ in the R_a/R_b and R substituents on the phenylpyridine and the other heterocyclic multiaromatic ligands, respectively, which can cover a wide range of substituents (e.g. halogens, aliphatic and aromatic groups, amines, nitro groups, and so on). For all the complexes, the yields of the reactions are strictly related to the number of substituents on the phenyl or pyridine rings of the ligands indicated as *a* or *b*.[40,41] The fact that higher yields are obtained when the value of *a* and *b* is in the range 0–2 can be ascribed to a combination of factors, mainly related to solubility in the reaction media or to deactivating effects.

Cl_2, Br_2,and I_2, *N*-halosuccinimides, or interhalogens (e.g. FCl, BrF, IF, BrCl, ICl) were used as halogenating agents in combination with a base (e.g. amines, carbonate, or salts of carboxylic acids) from 1:1 to 1:100 ratio. In some cases, Lewis acids such as AlX_3, FeX_3, ZnX_2, and SnX_4 (X = Cl or Br) were added (from 1:0.1 to 1:0.0001 ratios). The reactions were performed in both protic and aprotic solvents, with alcohols as the most used. Importantly, mild temperatures (10–60 °C) are sufficient for these reactions to occur. Depending on the system, reaction times from 1 to 40 h were applied to obtain good yields. Several complexes containing mixed ligand systems or dinuclear systems have been prepared as well (**59**–**62** in Scheme 13).[40]

Formylation is another organic transformation that was performed on the σ-aryl organometallic complexes **51** and **53** (Scheme 12). Regioselective substitution at the position(s) *para* to the $M–C_{ipso}$ bond was achieved in yields of 70–90 % by using *N*-methylformamide, *N*,*N*-dimethylformamide, and *N*-methylformanilide as formylating agents in combination with $POCl_3$ or $SOCl_2$ in 1:1 or 100:1 ratio.[42] As is the case with the halogenation reactions, the regioselectivity in formylation reactions has been attributed to the activating and directing effects of the metal center.

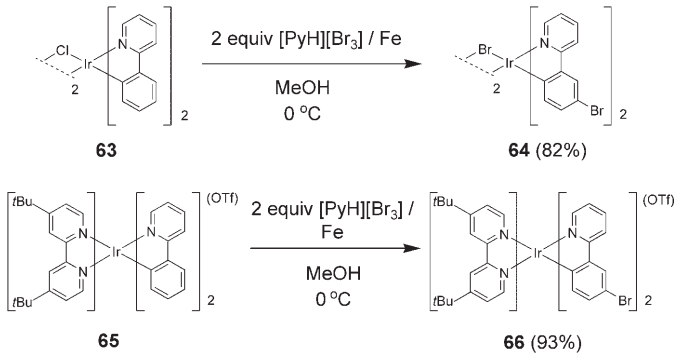
Stoessel et al. studied the selective functionalization of the *para* positions in more detail by control of the stoichiometric amounts of formylating agents used, with *n* equivalents leading to *n*-fold-substituted complexes as the only products.



Scheme 13. M = Rh, Ir; X = F, Cl, Br, I, CHO; Y = O, S, Se; Z = CO, nitrile, NR_3, PR_3, AsR_3, stilbene, heterocyclic groups; R = H, F, Cl, Br, NO_2, CN, alkyl, alkoxy, aryl, heterocyclic, and polyaromatic groups; *a* = 0–4 (better yields with 0–2); *b* = 0–3 (better yields with 0, 1); *n* = 0–2.

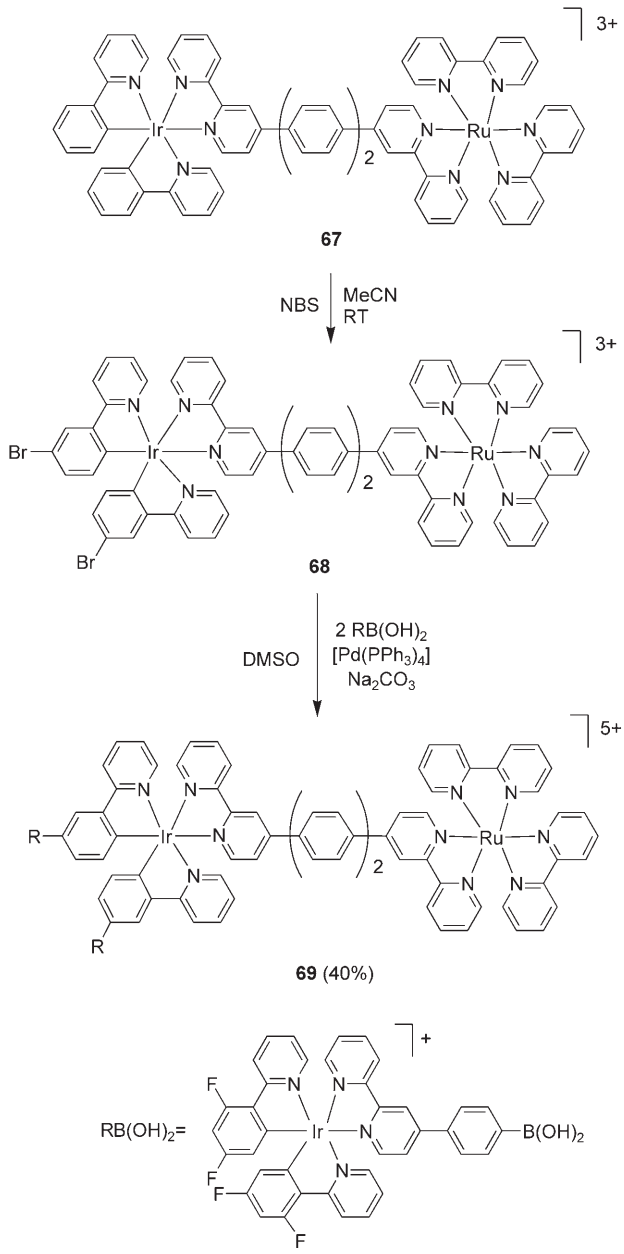
No cleavage of the M–C σ bonds was observed in any of the examples.[42] Some of the compounds prepared in this way have been used as monomers for the subsequent synthesis of conjugated polymers or have been incorporated into copolymers such as polyfluorene, polyspirobifluorene, and polyparaphenylene, leading to new materials with interesting optical and electronic properties.[42]

A few successful examples of further functionalization reactions for **52** and **54** are the Suzuki coupling and the Buchwald–Hartwig amination reaction.[42] For example, **52** and **54** react with diarylamines, yielding a series of complexes bearing the diarylamino group at the *para* position. These compounds find application as active compounds in electronic materials such as molecular switches and thin-film transistors.[43] The complexes bearing a formyl group reacted further with phosphonium salts in a Wittig reaction, or were converted into Schiff bases by reaction with amines, leading to optically or electronically interesting materials.[43] It is worth mentioning that the regioselective electrophilic bromination can also be applied to dimetallic complexes incorporating cyclometalated phenylpyridine units coordinated to an iridium(III) center.

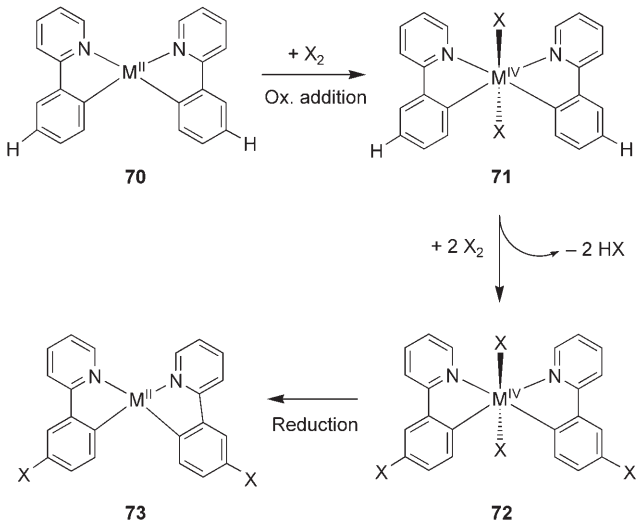


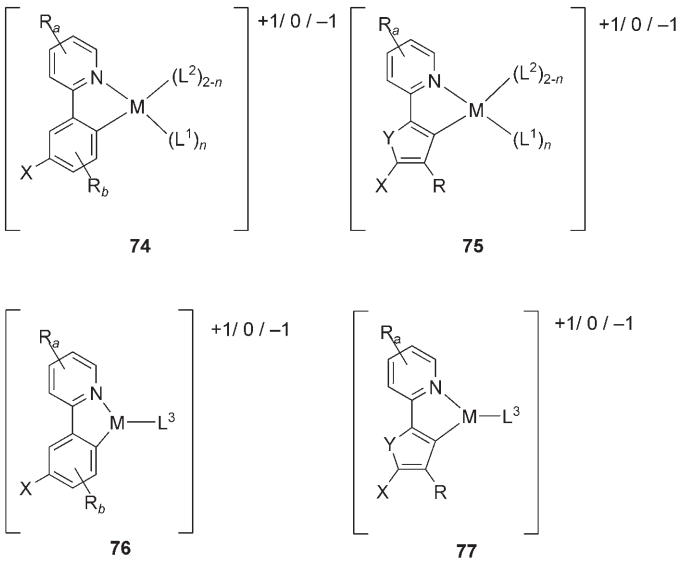
Scheme 14.

Cheung et al. have brominated the Ir^{III} complexes [{Ir(ppy)$_2$(μ-Cl)}$_2$] (**63**) and [Ir(ppy)$_2$(4,4′-*t*Bu-2,2′-bpy)](OTf) (**65**; ppy = 2-phenylpyridine) with pyridinium tribromide in the presence of iron powder, affording the complexes [{Ir(4-Br-ppy)(μ-Br)}$_2$] (**64**) and [Ir(4-Brppy)$_2$(4,4′-*t*Bu-2,2′-bpy)](OTf) (**66**), respectively (Scheme 14).[44] In the bromination of **65** also [{Ir(4-Br-ppy)(py)(μ-Br)}$_2$] was formed as a minor product, which could be separated by fractional crystallization. Both **64** and **66** have been successfully employed in



Scheme 15.





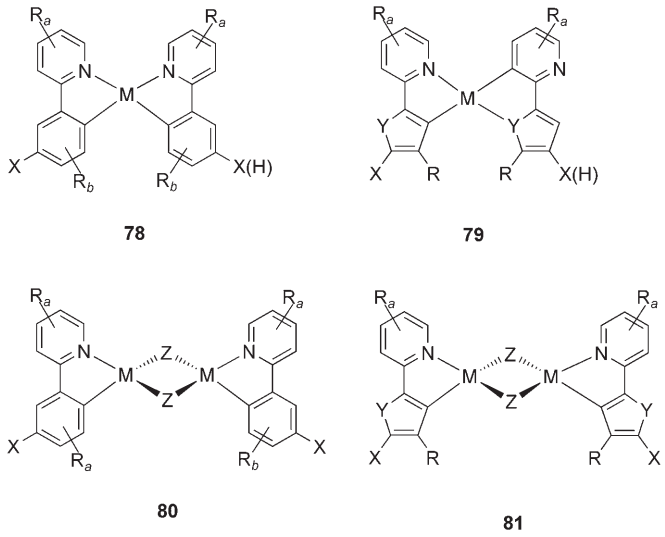
Scheme 16.

subsequent cross-coupling reactions with aryl boronic acids, ethynylstannane, and butynol.[44]

Williams et al. treated the dinuclear Ru–Ir complex **67** with two equivalents of NBS in acetonitrile at room temperature for 18 h to give the building block **68**. The latter undergoes cross-coupling reactions with different partners, allowing the preparation of tetrametallic assemblies such as **69** (Scheme 15).[45]

Very recent investigations undertaken by Stoessel et al. have focused on the synthesis of organopalladium(II) and organoplatinum(II) phosphorescent emitters containing functionalized heterocyclic multiaromatic ligands, which can be used as active components in the electronic industry.[46] Importantly, the reported work aims to clarify the mechanism of the direct halogenation. The regioselective halogenation of both ligands coordinated to the metal centers is achieved by using three equivalents of a halogenating agent (X_2; X = Cl, Br, I) in combination with a reducing agent. The proposed mechanism (Scheme 16) consists of an oxidative addition of the first equivalent of X_2 to the metal center in the square-planar complex **70**. Subsequent reaction of the proposed octahedral intermediate species **71** with two equivalents of halogenating agent leads to a regioselective substitution of the cyclometalated ligand at the *para* position relative to the metal center. Reduction of the intermediate **72** gives the desired complex **73** in high yield. The described synthetic procedure proved to be highly efficient and versatile for the selective preparation of a wide range of mono- and di-*ortho*-metalated organopalladium(II) and organoplatinum(II) complexes.[46]

Similarly to previously described procedures for the functionalization of Rh^{III} and Ir^{III} complexes, a large variety of substituted cyclometalated and ancillary ligands, halogenating and reducing agents, solvents, and reaction conditions have been successfully applied. In Scheme 17, a schematic representation of the obtained species is presented.



Scheme 17. M = Pd, Pt; X = Cl, Br, I; Y = O, S, N; R = H, F, Cl, Br, I, NO_2, CN, alkyl, alkoxy, mono- and polyaromatic ring systems; L^1 = neutral ligand; L^2 = monoanionic monodentate ligand; L^3 = neutral, mono-, or dianionic bidentate ligand; *a* = 0–4 (better yields with 0–2); *b* = 0–3 (better yields with 0–2).

4. Metal-Mediated Formation of Dinuclear Cyclometalated Ru^{II} and Os^{II}–Polypyridine Complexes

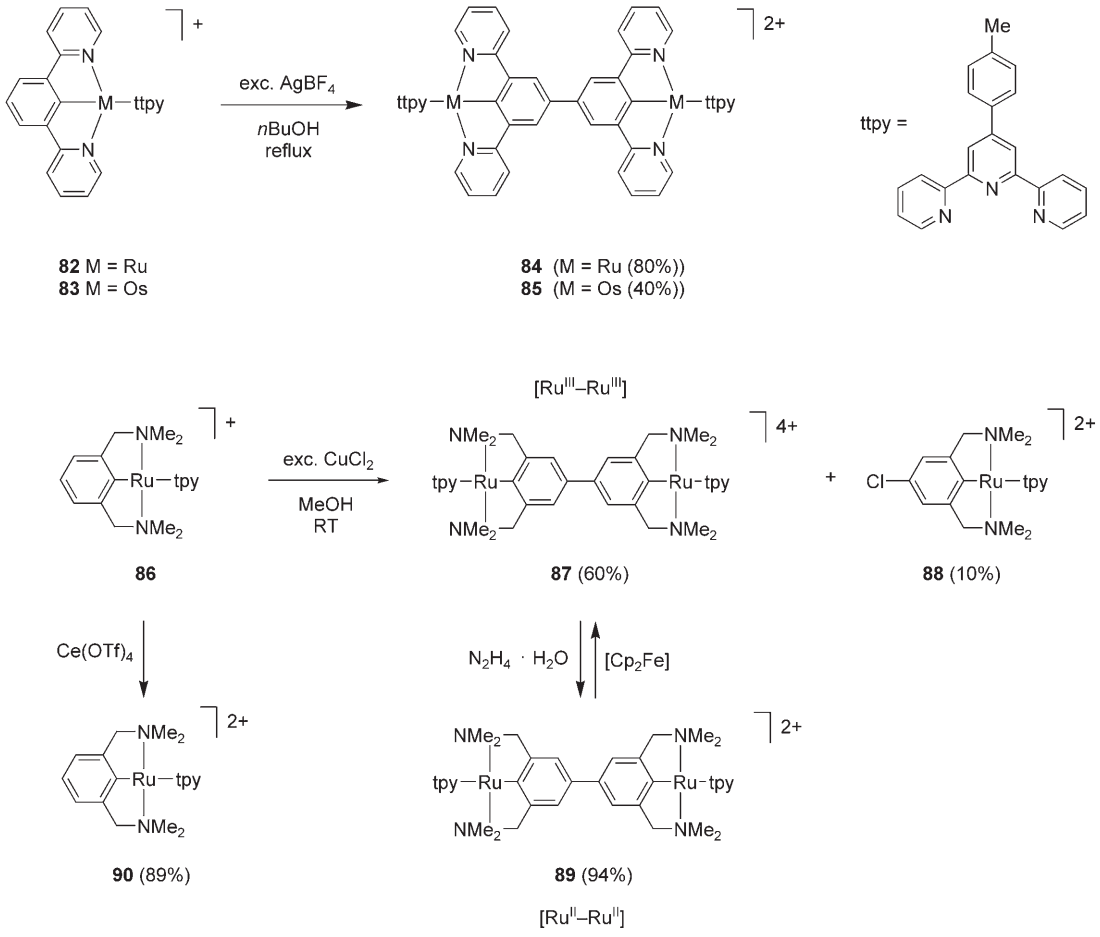
Ru- and Os-based building blocks connected by various types of homo- or heteroditopic bridging ligands (e.g. cyanides,[47] DNA,[48] polypeptides,[49] aliphatic chains,[50] *p*-phenylenevinylene oligomers,[51] polyenes,[52] polyalkynes,[53] polyphenylenes,[54] polyphenylalkynes,[55] or polythiophene units[56]) have been employed for the construction of dinuclear systems possessing interesting redox and photophysical properties.

In particular, dinuclear species containing ruthenium termini bridged by unsaturated carbon ligands are of great interest. Their reversible redox chemistry and easy accessibility of mixed-valence species make the use of these

complexes for the construction of organometallic polymers,[57] third-order nonlinear optical materials,[58] and molecular electronics[37,59] rather attractive. In this context, three different synthetic approaches have been applied for the preparation of dinuclear ruthenium species containing bis(polypyridine)[60] and bis(cyclometalated)[61] bridging ligands.

The first approach is based on the initial synthesis of bridging and terminal ligands. Coordination of the terminal ligands to the metal centers previously introduced, simultaneously or sequentially, at each site of the bridging ligand can give symmetrical or unsymmetrical dinuclear complexes.[62] The second strategy consists of a cross-coupling reaction between a diboronic acid derivative and a halogenated metal-containing building block. It has to be pointed out that in the case of organometallic building blocks, their halogenation is often conveniently carried out by using the procedures presented in the previous paragraphs. The third strategy involves organoruthenium building blocks containing monoanionic, cyclometalated ligands.[63] In such species, the *para* position with respect to the M–C_{aryl} σ bond is again activated, in this instance toward C–C oxidative coupling in the presence of a large excess of a strong oxidant. Sauvage and co-workers were the first to report the synthesis of the dinuclear complexes **84** (80%) and **85** (40%) by treating mononuclear **82** and **83** with an excess of $AgBF_4$ in refluxing *n*BuOH (Scheme 18).[63] The mechanism of this reaction is not completely clear, but it is likely to involve radicals located at the 4′-position of the central ring of **82** and **83**. Theoretical calculations showed that the HOMO of the monomer $[Ru(dpb)(tpy)]^{2+}$ (dpb = 1,3-di-*o*-pyridylbenzene) is mainly located at the ruthenium center and partly on the phenyl ring in *ortho* and in *para* position with respect to the metal center.[64] Since the dinuclear species is formed upon oxidative coupling, it can be assumed that oxidation of the Ru^{II} center to Ru^{III} generates a considerable unpaired-electron density at the *para* position, so that the radical coupling occurs in association with a deprotonation process.[63]

The excess Ag^{I} salt in the reaction mixture, as well as the presence of oxygen, turned out to be crucial to obtain these dimers in high yield. Interestingly, this reaction cannot be carried out with the free ligand under the same reaction conditions. Once the phenyl ring of the cyclometalated ligand is bonded to the Ru^{II} center, the position *para* to the M–C σ bond becomes activated toward oxidative coupling. Thus, this activation is strictly related to the electronic properties of the metal center. In fact, the analogous Os^{II} dinuclear complex **85** is obtained, albeit in very low yield, from the monomer $[Os(dpb)(ttpy)](PF_6)$ (**83**) under identical conditions.[63] Remarkably, this coupling reaction is highly selective since no other products than those involving the 4′-position of



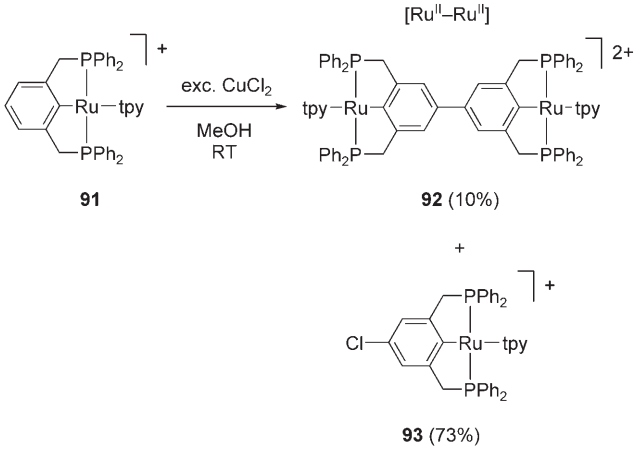
Scheme 18.

the dpb ligand could be detected. Use of stronger oxidants such as Ce^{IV} salts resulted in decomposition of both **82** and **83**.[63] However, surprisingly, the presence of O_2 in the reaction mixture gave the dinuclear complex **84** in higher yield.

Nearly simultaneously with the publication by Sauvage and co-workers, van Koten et al. reported on the preparation of the diamagnetic dinuclear 34-electron complex $[Ru^{III}_2(4,4'\text{-}\{C_6H_2(CH_2NMe_2)_2\text{-}2,6\}_2(tpy)_2](CuCl_2)_4$ (**87**)[65] This complex was synthesized by the Cu^{II}-mediated oxidative coupling of the mononuclear complex $[Ru^{II}\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}(tpy)]Cl$ (**86**, Scheme 18) containing the NCN pincer ligand. Interestingly, the *para*-chlorinated Ru^{III} monomeric complex **88** is also formed as a minor compound (10%). In contrast to the coupling reactions with Ag^I salts, the Cu^{II}-mediated formation of the covalent C–C bond in **87** is accompanied by the oxidation of both ruthenium centers. If $CuCl_2$ is replaced by $AgBF_4$ or stronger oxidants such as Ce^{IV} salts, complex **86** is quantitatively converted into the monomeric complex $[Ru^{III}\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}(tpy)]^{4+}$ (**90**).[65]

The mechanism of this process clearly involves activation of the aromatic C–H bond of the NCN pincer ligand in **86** that is *para*-positioned with respect to the $Ru\text{–}C_{ipso}$ σ bond. However, the fact that the C–C coupling reaction does not take place in the absence of Cu^{II}, or in aqueous medium, led to the conclusion that the mechanism of the reaction must involve heteronuclear organocopper intermediates. These intermediates have not yet been isolated or identified. It has been proposed that the first step of the reaction must involve the oxidation of the ruthenium center in **86** and the formation of Cu^I ions. Oxidation of the ruthenium center results in an activation of the *para* position, which reacts further with a copper metal center to give complex cluster aggregates involving combinations of Cu^I, Cu^{II}, and halides ions. Subsequently, as proposed for arylcopper aggregates,[66] reaction of these inner sphere-activated complexes with $CuCl_2$ gives $\{(NCN)Ru^{III}(tpy)\}$-containing radicals that collapse to give dinuclear species. Alternatively, they undergo a halide ion transfer oxidation[67] and Cu^ICl and species such as **88** are formed.

More recently, the reactivity of the mononuclear complex $[Ru^{II}(PCP)(tpy)]Cl$ (**91**, Scheme 19), containing the tridentate coordinating monoanionic PCP pincer ligand $[C_6H_3(CH_2PPh_2)_2\text{-}2,6]^-$, toward $CuCl_2$ was investigated.[68] Interestingly, its higher oxidation potential[69] compared to that of **86** gives rise to a different reactivity under the same experimental conditions. Analytical data proved that the major product formed in this case is the mononuclear, *para*-chlorinated complex **93**. The dinuclear complex $[Ru^{III}_2(4,4'\text{-}\{C_6H_2(CH_2PPh_2)_2\text{-}2,6\}_2(tpy)_2](CuCl_2)_4$ (**92**) is obtained only in low yield (ca. 10%).[68] These results suggest that the enhanced π-accepting character of the phosphorus atoms of the PCP pincer ligand in **91**, with respect to the "hard" σ-donor character of the amine nitrogen atom of the NCN pincer ligand in **86**, is the main controlling factor in the activation of the *para* position and, in turn, in the formation of dinuclear complexes in the presence of $CuCl_2$. However, the simultaneous formation of the chloro-functionalized complexes **88** and **93** indicates that the *para* positions in **86** and **91** are somewhat activated towards substitution, similarly to other cyclometalated Ru^{II} compounds presented in the previous sections of this review (Section 3). The photophysical and redox properties of the dimetallic complexes **84**,[64] **85**,[64] **87**,[65] and **92**[68] and of the mixed-valence species generated from their partial oxidation or reduction, have been subject of detailed studies. However, to the best of our knowledge, the metal-mediated oxidative C–C coupling with unfunctionalized organonometallic substrates is a synthetic approach still relatively unexplored.



Scheme 19.

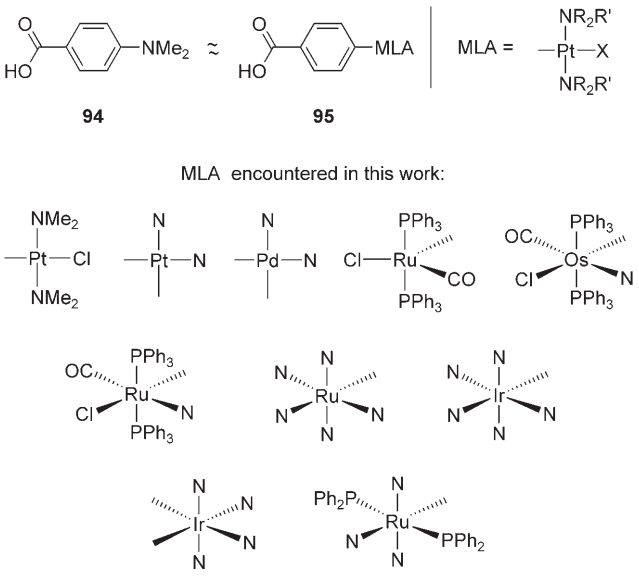
5. Conclusions and Outlook

Organic transformations on σ-aryl organometallic complexes mediated by the presence of an ancillary transition-metal center can roughly be divided into two categories: 1) electrophilic aromatic substitution on the aryl ligand and 2) oxidative C–C coupling of the unactivated C–H aryl bond. To date, only a limited number of investigations have been carried out directed to gain insight in the mechanistic aspects of these reactions. Probably, this situation is related to the fact that these synthetic approaches are in their infancy, and work was essentially directed toward the optimization of the reaction conditions. Direct electrophilic substitution of metalated ligands is, at the moment, limited to halogenation, nitration, sulfonation, acylation, and formylation. The presence of a metal center in the substrate induces in both cases a regioselective substitution to the organic ligand at the *para* position relative to the M–C σ bond. Importantly, it was demonstrated that in most cases the *para* position is the only position subjected to functionalization and that the free ligands do not undergo the same transformations under identical reaction conditions. It has been proposed that electrophilic substitution at the *para* position relative to the M–C σ bond is due to an enhanced electron density at this position, which can be considered as pushed away from the metal center. However, in some instances, a metal concurrently activates the *ortho* position as well. In some cases, when the *para* position is unavailable, the formation of *ortho*-substituted products is also observed. Moreover, when an excess of reagent is used, disubstitution at both *para* and *ortho*

positions may take place. Thus, stoichiometric control of substrate and reagents plays an important role.

Although the use of aggressive reagents is thought to cause cleavage of the M–C σ bond, it was shown through a selected number of cases that a variety of organometallic compounds can easily be handled under these reaction conditions. In some cases, the stability of the organometallic building block is due to a combination of the presence of a strong M–C σ bond and *ortho* chelation, which provides the additional stabilization by formation of a metallacycle. In contrast to the growing number of publications on dinuclear Ru^{II} and Os^{II} complexes containing cyclometalated ligands, the formation of such species by an oxidative C–C coupling of the *para*-carbon atoms of the corresponding mononuclear Ru^{II} and Os^{II} complexes mediated by Ag^{I} or Cu^{II} salts is relatively unexplored. This synthetic strategy represents an interesting alternative method that merits more attention. From the current literature it is obvious that the class of organic transformations described in this review are increasingly used to produce, from activated organometallic building blocks, larger molecular architectures with interesting redox and photophysical properties. In this respect, this review provides an overview on the work reported up to now, with the aim of encouraging the application of these strategies in organometallic synthesis. Moreover, the simplicity of most of the procedures as well as the good yields obtained suggest that these methodologies could also constitute a novel route to unusually substituted organic materials that are difficult to prepare by other means and can act as new ligands or, upon metal removal, as novel compounds in their own right.

It is interesting to approach the chemistry that has been highlighted in the present paper as an organic synthetic chemist who is simply interested in the functionalization of an aryl ring that has a σ-bonded metal–ligand array (MLA) as a substituent. The question that would arise then is: Provided that the σ-bonded MLA is stable during the electrophilic substitution, can the control of this group allow one to take advantage of its influence in organic synthesis? To answer this question in a qualitative way, we would have to understand the inductive and mesomeric effects of such an MLA on an aryl ring. In this vein, we measured the acidity of a benzoic acid derivative bearing a platinum bis(*tert*-amino) halide group {$PtCl(R_2R'N)_2$} (**95**, Scheme 20) in the *para* position by using the classical Hammett correlation. The obtained data indicate that the *para*-{$PtCl(R_2R'N)_2$} group exerts an electron-releasing effect comparable to that of an NH_2 or NMe_2 group (**94**; $\sigma_p = -1.18$ (MeOH), -0.72 (1:1 H_2O/MeOH)).[27d] In the examples reported in this review, we have encountered that the *ortho*/*para* orientation of a MLA substituent (M = Ru, Os, Ir, Pt, Pd) σ-bonded to an aryl ring reacts in accord with the usual, well-documented *ortho*/*para*-directing effect of a Me_2N group in the course of electrophilic substitution. The pathway through which the MLA substituents affect the *para* and *ortho* position of an Ar–H ring during substitution needs further comment. In a qualitative way, we can argue that the polarity of the M–C_{ipso} bond places a partial negative charge on the C_{ipso}. This negative charge can be delocalized throughout the aryl ring in a similar way as the N lone pair of an NMe_2 group influences an electrophilic substitution pathway. Moreover, changing the nature of the R substituents on an NR_2 group modulates its mesomeric and inductive properties, and this effect is complemented in the MLA system. For example, by changing the ligand *trans* to C_{ipso} in a square-planar MLA substituent, the negative charge on C_{ipso} can be altered through the *trans* influence and thus its effect on electrophilic processes. In Scheme 20, the various MLAs encountered in the present overview are summarized. For some of these MLAs we currently are measuring the Hammett parameter σ_{para} because this information can qualitatively assist in the design of reaction pathways for the direct transformation of aryl rings in these metal complexes.



Scheme 20. MLA = metal–ligand array.

Interestingly, in the discussion of the various C–C coupling reactions (see Section 4) we encountered a unique property of an MLA that strictly does not have a counterpart in organic chemistry ({Ru(tpy)} in **86**, Scheme 18). When an MLA substituent comprises a metal center that has multiple stable even and odd formal oxidation states, a selective one-electron switch can occur, affording an odd-electron MLA substituent instead of an even-electron substituent. The odd-electron MLA can have its electron density either fully localized on the metal center or can have this electron density distributed over both the metal center and the arene ring. Following these qualitative ideas, we have recently designed a novel route for "push–pull" stilbenoid NLO materials that have one of the organic substituents replaced by an MLA with electron-releasing properties.[70]

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[1] a) C. Elschenbroich, A. Salzer, *Organometallics: A Concise Introduction*, 2nd ed., VCH, New York, **1989**; b) R. H. Crabtree, *The Organometallic Chemistry of Transition Metals*, 2nd ed., Wiley, New York, **1988**.

[2] a) T. J. Kealy, P. L. Pauson, *Nature* **1951**, *168*, 1039; b) P. Laszlo, R. Hoffmann, *Angew. Chem.* **2000**, *112*, 127; *Angew. Chem. Int. Ed.* **2000**, *39*, 123.

[3] G. Wilkinson, M. Rosenblum, M. C. Whitting, R. B. Woodward, *J. Am. Chem. Soc.* **1952**, *74*, 2125.

[4] a) E. O. Fischer, W. Pfab, *Z. Naturforsch. B* **1952**, *7*, 377; b) E. O. Fischer, R. Jira, *J. Organomet. Chem.* **2001**, 7, 637.

[5] J. Chatt, L. A. Duncanson, *J. Chem. Soc.* **1953**, 2939.

[6] a) G. W. Parshall, R. E. Putscher, *J. Chem. Educ.* **1986**, *63*, 189; b) *Applied Homogeneous Catalysis with Organometallics Compounds* (Eds.: B. Cornils, W. A. Herrmann), **1997**; c) R. Whyman, *Applied Organometallic Chemistry and Catalysis*, Oxford University Press, Oxford, **2001**.

[7] a) *Mechanisms of Inorganic and Organometallic Reactions*, *Vol. 1–4* (Ed.: M. V. Twigg), Plenum, New York, **1983–1986**; b) B. J. Burger, B. D. Santarsiero, M. S. Trimmer, J. E. Bercaw, *J. Am. Chem. Soc.* **1988**, *110*, 3134; c) J. A. Finch, E. V. Anslyn, R. H. Grubbs, *J. Am. Chem. Soc.* **1988**, *110*, 2406; d) H. E. Bryndza, P. J. Domaille, R. A. Paciello, J. E. Bercaw, *Organometallics* **1989**, *8*, 379.

[8] a) R. G. Pearson, *Chem. Rev.* **1985**, *85*, 41; b) L. E. Schock, T. J. Marks, *J. Am. Chem. Soc.* **1988**, *110*, 7701; c) J. A. Labinger, J. E. Bercaw, *Organometallics* **1988**, *7*, 926.

[9] a) A. Boudier, L. O. Bromm, M. Lotz, P. Knochel, *Angew. Chem.* **2000**, *112*, 4584; *Angew. Chem. Int. Ed.* **2000**, *39*, 4415, and references therein; b) P. Knochel, E. Hupe, W. Dohle, D. M. Lindsay, V. Bonnet, G. Quéguiner, A. Boudier, F. Kopp, S. Demay, N. Seidel, M. I. Calaza, V. A. Vu, I. Sapountzis, T. Bunlaksananusorn, *Pure Appl. Chem.* **2002**, *74*, 11.

[10] Representative examples: a) J. A. Moulijn, R. A. Sheldon, H. van Bekkum, P. W. N. M. van Leeuwen, *Catalysis: An Integrated Approach to Homogeneous, Heterogeneous and Industrial Catalysis*, 2nd ed. (Eds.: J. A. Moulijn, P. W. N. M. van Leeuwen, R. A. van Santen), Elsevier, Amsterdam, **1995**; b) H. Brunner, *Applied Homogeneous Catalysis with Organometallic Compounds*, *Vol. 1* (Eds.: B. Cornils, W. A. Herrmann), VCH, Weinheim, **1996**; c) Y. Hisaeda, O. Hayashida, *Chem. Rev.* **1996**, *96*, 721.

[11] a) P. Nguyen, P. Gomez-Elipe, I. Manners, *Chem. Rev.* **1999**, *99*, 1515; b) V. Chandreskhar, *Inorganic and Organometallic Polymers*, Springer, Berlin, **2004**.

[12] P. A. Chase, R. J. M. Klein Gebbink, G. van Koten, *J. Organomet. Chem.* **2004**, *689*, 4016.

[13] a) M. Albrecht, M. Lutz, A. L. Spek, G. van Koten, *Nature* **2000**, *406*, 970; b) K. J. Franz, N. Singh, S. J. Lippard, *Angew. Chem.* **2000**, *112*, 2194; *Angew. Chem. Int. Ed.* **2000**, *39*, 2120.

[14] a) K. Severin, R. Bergs, W. Beck, *Angew. Chem.* **1998**, *110*, 1722; *Angew. Chem. Int. Ed.* **1998**, *37*, 1635; b) D. R. van Staveren, N. Metzler-Nolte, *Chem. Rev.* **2004**, *104*, 5931; c) S. Debasis, S. Sudeshna, P. Subrata, R. Manju, S. Michele, S. Amitabha, *J. Organomet. Chem.* **2005**, *690*, 5581.

[15] S. Leininger, B. Olenyuk, P. J. Stang, *Chem. Rev.* **2000**, *100*, 853.

[16] a) S. A. Hudson, P. M. Maitlis, *Chem. Rev.* **1993**, *93*, 861; b) C. Imrie, P. Engelbrecht, C. Loubser, C. W. McCleland, *Appl. Organomet. Chem.* **2001**, *15*, 1.

[17] Some representative examples: a) P. Reveco, R. H. Schmehl, W. R. Cherry, F. R. Fronczek, J. Selbin, *Inorg. Chem.* **1985**, *24*, 4078; b) J. Vincente, A. Arcas, M. V. Borrachero, E. Molíns, C. Miravitlles, *J. Organomet. Chem.* **1992**, *441*, 487; c) J. Vincente, J. A. Abad, J. Gil-Rubio, *Organometallics* **1993**, *12*, 4151; d) Y. J. Kim, R. Sato, T. Maruyama, K. Osakada, T. Yamamoto, *J. Chem. Soc. Dalton Trans.* **1994**, 943; e) H. P. Dijkstra, P. Steenwinkel, D. M. Grove, M. Lutz, A. L. Spek, A. J. Canty, G. van Koten, *Angew. Chem.* **1999**, *111*, 2321; *Angew. Chem. Int. Ed.* **1999**, *38*, 2186; f) J. Vincente, J. A. Abad, A. D. Frankland, M. C. Ramírez de Arellano, *Chem. Eur. J.* **1999**, *5*, 3066; g) H. P. Dijkstra, M. Albrecht, G. van Koten, *Chem. Commun.* **2002**, 126.

[18] a) D. E. Bublitz, K. L. Rinehart, *Organic Reactions*, *Vol. 17* (Ed.: W. G. Dauben), Wiley, New York, **1969**; b) E. Puciová, E. Solcaniová, S. Toma, *Tetrahedron* **1994**, *50*, 5765; c) A. F. Cunningham, *Organometallics* **1997**, *16*, 1114.

[19] a) D. M. Grove, G. van Koten, H. J. C. Ubbels, *Organometallics* **1982**, *1*, 1366; b) M. Albrecht, A. L. Spek, G. van Koten, *J. Am. Chem. Soc.* **2001**, *123*, 7233.

[20] G. R. Clark, C. E. L. Headford, W. R. Roper, L. J. Wright, V. P. D. Yap, *Inorg. Chim. Acta* **1994**, *220*, 261.

[21] a) J. Vincente, J. A. Abad, J. A. Sanchez, *J. Organomet. Chem.* **1988**, *352*, 257; b) W. A. Herrmann, C. Broßmer, T. Priermeier, K. Öfele, *J. Organomet. Chem.* **1994**, *481*, 97.

[22] J. B. Menke, *Recl. Trav. Chim. Pays-Bas.* **1925**, *44*, 141.

[23] a) M. S. Kharasch, H. S. Isbell, *J. Am. Chem. Soc.* **1931**, *53*, 3053; b) R. P. Shibaeva, L. P. Rozenberg, R. M. Lobkovskaya, A. E. Shilov, G. B. Shul'pin, *J. Organomet. Chem.* **1981**, *220*, 271.

[24] P. Braunstein, R. J. H. Clark, *Inorg. Chem.* **1981**, *13*, 271.

[25] G. R. Clark, C. E. F. Rickard, W. R. Roper, L. J. Wright, V. P. D. Yap, *Inorg. Chim. Acta* **1996**, *251*, 65.

[26] M. K. Lau, Q. F. Zhang, J. L. C. Chim, W. T. Wong, W. H. Leung, *Chem. Commun.* **2001**, 1478.

[27] a) G. W. Parshall, *J. Am. Chem. Soc.* **1974**, *96*, 2360; b) J. Manna, C. J. Kuehl, J. A. Whiteford, P. J. Stang, *Organometallics* **1997**, *16*, 1897; c) M. Q. Slagt, R. J. M. Klein Gebbink, M. Lutz, A. L. Spek, G. van Koten, *J. Chem. Soc. Dalton Trans.* **2002**, 2591; d) M. Q. Slagt, G. Rodríguez, M. M. P. Grutters, R. J. M. Klein Gebbink, W. Klopper, L. W. Jenneskens, M. Lutz, A. L. Spek, G. van Koten, *Chem. Eur. J.* **2004**, *10*, 1331.

[28] G. Rodríguez, M. Albrecht, J. Schoenmaker, A. Ford, M. Lutz, A. L. Spek, G. van Koten, *J. Am. Chem. Soc.* **2002**, *124*, 5127.

[29] a) G. Guillena, G. Rodríguez, G. van Koten, *Tetrahedron Lett.* **2002**, *43*, 3895; b) G. Guillena, K. M. Halkes, G. Rodríguez, G. D. Batema, G. van Koten, J. P. Kamerling, *Org. Lett.* **2003**, *5*, 2021; c) D. Beccati, K. M. Halkes, G. D. Batema, G. Guillena, A. Carvalho de Souza, G. van Koten, J. P. Kamerling, *ChemBioChem* **2005**, *6*, 1196.

[30] A. M. Clark, C. E. F. Rickard, W. R. Roper, L. J. Wright, *Organometallics* **1998**, *17*, 4535.

[31] J. L. Butler, M. Gordon, *J. Heterocycl. Chem.* **1975**, *12*, 1015.

[32] A. M. Clark, C. E. F. Rickard, W. R. Roper, L. J. Wright, *Organometallics* **1999**, *18*, 2813.

[33] R. Forsyth, F. L. Pyman, *J. Chem. Soc.* **1926**, *129*, 2912.

[34] A. M. Clark, C. E. F. Rickard, W. R. Roper, L. J. Wright, *J. Organomet. Chem.* **2000**, *598*, 262.

[35] a) M. A. Baldo, M. E. Thompson, S. R. Forrest, *Nature* **2002**, *403*, 750; b) S. Lamansky, P. I. Djurovich, D. Murphy, F. Abdel-Razzaq, H. E. Lee, C. Adachi, P. E. Burrows, S. R. Forrest, M. E. Thompson, *J. Am. Chem. Soc.* **2001**, *123*, 4304; c) Md. K. Nazeeruddin, R. Humphry-Baker, D. Berner, S. Rivier, L. Zuppiroli, M. Graetzel, *J. Am. Chem. Soc.* **2003**, *125*, 8790; d) A. B. Tamayo, B. D. Alleyne, P. I. Djurovich, S. Lamanski, I. Tsyba, N. N. Ho, R. Bu, M. E. Thompson, *J. Am. Chem. Soc.* **2003**, *125*, 7377.

[36] C. Coudret, S. Fraysse, J. P. Launay, *Chem. Commun.* **1998**, 663.

[37] S. Fraysse, C. Coudret, J. P. Launay, *J. Am. Chem. Soc.* **2003**, *125*, 5880.

[38] S. Fraysse, C. Coudret, *Tetrahedron Lett.* **1999**, *40*, 9249.

[39] a) V. Balzani, F. Scandola, *Supramolecular Photochemistry*, Ellis Horwood, Chichester, **1991**; b) V. Balzani, M. Juris, S. Venturi, S. Campagna, S. Serroni, *Chem. Rev.* **1996**, *96*, 759.

[40] a) P. Stoessel, H. Spreitzer, H. Becker, DE 101 09 027A1, **2002**; b) P. Stoessel, H. Spreitzer, H. Becker, WO 02/068435A1, **2002**;

c) P. Stoessel, I. Bach, H. Spreitzer, H. Becker, WO 03/084972A1, **2003**; d) P. Stoessel, I. Bach, H. Spreitzer, H. Becker, WO 026886A2, **2004**.
[41] P. Stoessel, I. Bach, H. Spreitzer, H. Becker, WO 2004/037836A1, **2004**.
[42] P. Stoessel, H. Spreitzer, H. Becker, WO 03/040160A1, **2003**.
[43] P. Stoessel, H. Spreitzer, H. Becker, DE 101 16 962A1, **2002**.
[44] K. M. Cheung, Q. F. Zhang, K. W. Chan, M. H. W. Lam, I. D. Williams, W. H. Leung, *J. Organomet. Chem.* **2005**, *690*, 2913.
[45] K. J. Arm, J. A. G. Williams, *Chem. Commun.* **2005**, 230.
[46] P. Stoessel, I. Bach, H. Spreitzer, WO 2004/041835A1, **2004**.
[47] R. Amadelli, R. Argazzi, C. A. Bignozzi, F. Scandola, *J. Am. Chem. Soc.* **1990**, *112*, 7099.
[48] a) P. J. Dandliker, R. E. Holmin, J. K. Barton, *Science* **1997**, *275*, 1465; b) S. O. Kelley, N. M. Jackson, M. J. Hill, J. K. Barton, *Angew. Chem.* **1999**, *111*, 991; *Angew. Chem. Int. Ed.* **1999**, *38*, 941, and references therein; c) A. Harriman, *Angew. Chem.* **1999**, *111*, 996; *Angew. Chem. Int. Ed.* **1999**, *38*, 945.
[49] a) J. R. Winkler, H. B. Gray, *Chem. Rev.* **1992**, *92*, 369; b) G. McLendon, R. Hake, *Chem. Rev.* **1992**, *92*, 481; c) B. Geisser, R. Alsfasser, *Inorg. Chim. Acta* **2003**, *344*, 102.
[50] a) G. L. Closs, J. L. Miller, *Science* **1988**, *240*, 440; b) P. Klan, P. J. Wagner, *J. Am. Chem. Soc.* **1998**, *120*, 2198.
[51] a) W. B. Davis, W. A. Svec, M. A. Ratner, M. R. Wasielewski, *Nature* **1998**, *396*, 60; b) SS. Liu, Q. Y. Hu, P. Xue, T. B. Wen, I. D. Williams, G. Jia, *Organometallics* **2005**, *24*, 769; c) J. Maurer, B. Sarkar, B. Schwederski, W. Karm, R. F. Winter, S. Zalis, *Organometallics* **2006**, *25*, 3701.
[52] G. Pickaert, R. Ziessel, *Tetrahedron Lett.* **1998**, *39*, 3497.
[53] a) A. Harriman, R. Ziessel, *Platinum Met. Rev.* **1996**, *40*, 26;A. Harriman, R. Ziessel, *Platinum Met. Rev.* **1996**, *40*, 72; b) D. Tzalis, Y. Tor, *J. Am. Chem. Soc.* **1997**, *119*, 852; c) G. Schermann, T. Grösser, F. Hampel, A. Hirsch, *Chem. Eur. J.* **1997**, *3*, 1105; d) U. Siemeling, U. Vorfeld, B. Neumann, H. G. Stammler, P. Zanello, F. Fabrizi de Biani, *Eur. J. Inorg. Chem.* **1999**, 1; e) A. El-ghayoury, A. Harriman, A. Khatyr, R. Ziessel, *Angew. Chem.* **2000**, *112, 191; Angew. Chem. Int. Ed.* **2000**, 39, 185.
[54] a) J. P. Sauvage, J. P. Collin, J. C. Chambron, S. Guillerez, C. Coudret, V. Balzani, F. Barigelletti, L. De Cola, L. Flamigni, *Chem. Rev.* **1994**, *94*, 993; b) B. Schlicke, P. Belser, L. De Cola, E. Sabbioni, V. Balzani, *J. Am. Chem. Soc.* **1999**, *121*, 4207.
[55] a) S. Huang, J. M. Tour, *Tetrahedron Lett.* **1999**, *40*, 3347; b) A. C. Benniston, V. Grosshenny, A. Harriman, R. Ziessel, *Dalton Trans.* **2004**, 1227; c) K. Onitsuka, N. Ohara, F. Takei, S Takahashi, *Dalton Trans.* **2006**, 3693.
[56] a) M. S. Vollmer, F. Würthner, F. Effenberger, P. Emele, D. U. Meyer, T. Stümpfig, H. Port, H. C. Wolf, *Chem. Eur. J.* **1998**, *4*, 260; b) S. Hencinas, L. Flamigni, F. Bargelletti, E. C. Constable, C. E. Housecroft, E. R. Schofield, E. Figgemeier, D. Fenske, M. Neuburger, J. G. Vos, M. Zehnder, *Chem. Eur. J.* **2002**, *8*, 137.
[57] T. Ren, *Organometallics* **2005**, *24*, 4854.
[58] a) W. J. Blau, H. J. Byrne, D. J. Cardin, A. P. Davey, *Non Linear Optics and Photonics* (Eds.: J. Messier, F. Kajar, P. Prasad, D. Ulrich), Kluwer, Dordrecht, **1991**, p. 391; b) N. J. Long, C. K. Williams, *Angew. Chem.* **2003**, *115*, 2690; *Angew. Chem. Int. Ed.* **2003**, *42*, 2586.
[59] C. Hortholary, C. Coudret, *J. Org. Chem.* **2003**, *68*, 2167.
[60] a) V. Grosshenny, R. Ziessel, *Tetrahedron Lett.* **1992**, *33*, 8075; b) J. P. Collin, P. Lainé, J. P. Launay, J. P. Sauvage, A. Sour, *J. Am. Chem. Soc.* **1993**, *115*, 434.
[61] M. Beley, S. Chodorowski-Kimmes, J. P. Collin, P. Lainé, J. P. Launay, J. P. Sauvage, *Angew. Chem.* **1994**, *106*, 1854; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1775.
[62] S. Chodorowski-Kimmes, M. Beley, J. P. Collin, J. P. Sauvage, *Tetrahedron Lett.* **1996**, *37*, 2963.
[63] M. Beley, J. P. Collin, J. P. Sauvage, *Inorg. Chem.* **1993**, *32*, 4539.
[64] C. Patoux, J. P. Launay, M. Beley, S. Chodorowski-Kimmes, J. P. Collin, S. James, J. P. Sauvage, *J. Am. Chem. Soc.* **1998**, *120*, 3717.
[65] a) J. P. Sutter, D. M. Grove, M. Beley, J. P. Collin, N. Veldman, A. L. Spek, J. P. Sauvage, G. van Koten, *Angew. Chem.*. **1994**, *106*, 1359; *Angew. Chem. Int. Ed.* **1994**, *33*, 1282; b) J. P. Sutter, M. Beley, J. P. Collin, N. Veldman, A. L. Spek, J. P. Sauvage, G. van Koten, *Mol. Cryst. Liq. Cryst.* **1994**, *253*, 215; c) P. Steenwinkel, D. M. Grove, N. Veldman, A. L. Spek, G. van Koten, *Organometallics* **1998**, *17*, 5647.
[66] a) G. van Koten, A. J. Leusink, J. G. Noltes, *J. Organomet. Chem.* **1975**, *84*, 117; b) G. van Koten, J. G. Noltes, *J. Organomet. Chem.* **1975**, *84*, 117.
[67] J. K. Kochi, *Organometallic Mechanisms and Catalysis*, Academic Press, New York, **1978**.
[68] M. Gagliardo, C. H. M. Amijs, M. Lutz, A. L. Spek, R. W. A. Havenith, F. Hartl, G. P. M. van Klink, G. van Koten, *Inorg. Chem.*, in press.
[69] M. Gagliardo, H. P. Dijkstra, P. Coppo, L. De Cola, M. Lutz, A. L. Spek, G. P. M. van Klink, G. van Koten, *Organometallics* **2004**, *23*, 5833.
[70] G. D. Batema, K. T. L. van de Westelaken, J. Guerra, M. Lutz, A. L. Spek, C. A. van Walree, C. de Mello Donegá, A. Meijerink, G. P. M. van Klink, G. van Koten, *Eur. J. Inorg. Chem.* **2007**, 1422.

