Recent Findings in Cyclometallation of *meta*-Substituted Aryl Ligands by Platinum Group Metal Complexes by $C_{aryl}-R$ Bond Activation ($R = H, CR_3, SiR_3$)

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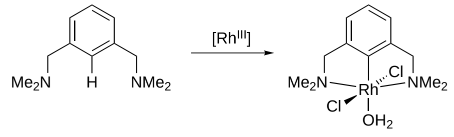
Abstract: Cyclometallation of aryl ligands with two donor substituents in the *meta*-positions occurs by $C_{aryl}-R$ bond activation and is facilitated by intramolecular coordination of these donor substituents. This procedure has been used for the preparation of a variety of platinum group metal organometallic complexes with interesting catalytic and electronic properties. Some recent findings are detailed.

Keywords: C–C activation · C–Si activation · C–H activation · metallacycles · metalations · palladium · platinum

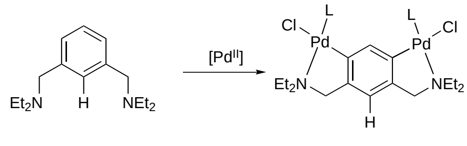
Transition metal complexes containing one or more metal–aryl bonds are becoming increasingly important in catalysis.[1] These compounds exhibit a wide range of reactivity encompassing dehydrogenation,[2] coupling,[1a] insertion[1b, c] and addition reactions.[3] Also, many metal–aryl compounds can be used to promote selective olefin polymerization.[4] In the last decade there has been considerable interest in the synthesis of these complexes by direct cyclometallation. This allows the use of simple *organic* starting materials and hence is much more economic than those reactions that require the use of expensive and air-sensitive organometallic precursors (e.g., RLi). The cyclometallation of arene ligands is usually promoted (by the chelate effect) by intramolecular coordination of donor groups on the ligand precursor prior to formation of the metal–carbon σ bond.[5a] Thermodynamically, the energy of the $C_{aryl}-R$ bond to be broken is related to the nature of the R group. The measured value of the C_6H_5-R ($R = H$) bond is 102 $kJ\,mol^{-1}$ with a much lower value for the same bond for toluene ($R = CH_3$; 63 $kJ\,mol^{-1}$).[5b] Although related values for phenylsilane (or phenyltrimethylsilane) are not known, comparable energies are found for a R_3C-CR_3 bond and the silyl analogue R_3C-SiR_3.[5c] This brief overview will concentrate on recent examples involving the direct cyclometallation (by $C_{aryl}-R$ bond cleavage or insertion; $R = H$, CR_3 or SiR_3) of aromatic ligands that contain two *meta*-positioned substituents bearing N-, S- or P-donor groups. Specifically, the formation of aryl complexes with the platinum group metals (e.g., Ru, Os, Rh, Ir, Pd and Pt) will be described.

Aromatic hydrocarbons that contain two sp^3 tertiary amine functionalities in the 1,3-positions have been shown to undergo aryl-cyclometallation selectively at C-2 by $C_{aryl}-H$ bond activation using, for example, rhodium compounds [Eq. (1)]. The products are Rh^{III} complexes in which the aryl ligand provides *N,C,N′*-terdentate coordination.[6] Macrocyclic aryldiamines also display this C–H bond activation behaviour.[7]



(1)

In general, other platinum group metal complexes do not undergo selective cyclometallation at C-2 of the 1,3-bis[(dimethylamino)methyl]benzene (NCN) ligand. However, the related aryldiamine 1,3-bis[(diethylamino)methyl]benzene can be cyclopalladated in an electrophilic reaction under special conditions, as reported by Trofimenko.[8] In this case, a 4,6-disubstituted bispalladium(II) complex is isolated instead of the expected mononuclear cyclometallated species [Eq. (2)]. A monopalladated product is assumed to be formed initially but as it is much more electron-rich than the free organic precursor, a facile second palladation reaction results. The structure of the final product suggests that only one of the N-donor substituents is coordinated prior to the



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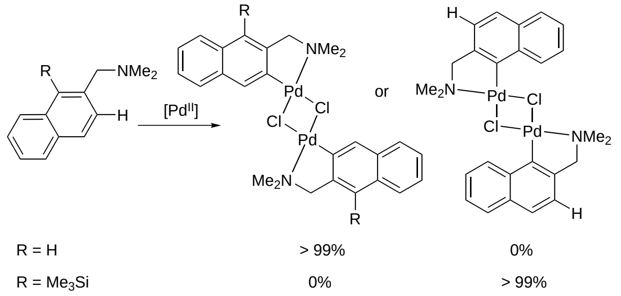
cyclometallation reaction. In terms of metallation, this would place the H atoms on C-4 and C-6 of the aromatic ring in the least sterically encumbered positions relative to the H atom on C-2.

If this central H atom is replaced by a $SiMe_3$ or $SnMe_3$ group, the ligand can be palladated selectively to afford mononuclear NCN-Pd^{II} complexes.[9] In this case the NCN ligand binds in a terdentate coordination mode and the most sterically demanding position of the aromatic ring is metallated (cf., [Eq. (2)]). This barrier is evidently overcome by the directional effect (and probably the leaving-group properties) of the $SiMe_3$ or $SnMe_3$ group. Valk et al. had previously studied the electrophilic palladation of $SiMe_3$-substituted 2-(dimethylamino)methylnaphthalenes [Eq. (3)].[10] This work had demonstrated that substitution of an aryl–H by a $SiMe_3$ group inverts the site selectivity of the palladation reaction from the naphthyl C-3 to C-1. The driving force is hypothesized to be facile C_{aryl}–Si bond cleavage. This approach has also been successfully applied in the synthesis of bridged bispalladium(II) complexes containing a dianionic ligand in which four CH_2NMe_2 groups are present on a single aromatic ring [Eq. (4)].[11]′



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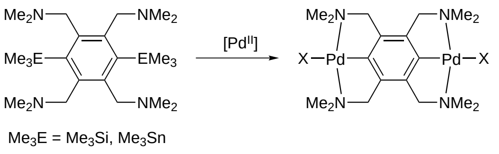


(4)

Earlier work by van Koten et al.[12] detailed the isolation of arenonium complexes that could be viewed as a representative of an intermediate in C_{aryl}–R cyclometallation. Figure 1 illustrates one of these arenonium complexes of Pt^{II} which resembles a potential mid-point in the C_{aryl}–Me activation of a bidentate *N,N′*- bound $[1,3\text{-}(Me_2NCH_2)_2\text{-}2\text{-}Me\text{-}C_6H_3]$ moiety.

Abstract in Dutch: *Cyclometallering van arylliganden met twee donorsubstituenten in de meta-posities vindt plaats via C_{aryl}-R bandactivering en wordt vergemakkelijkt door intramoleculaire coördinatie van deze donorsubstituenten. Deze procedure is gebruikt voor de synthese van een variëteit aan platina-groep organometaalcomplexen met interessante katalytische en electronische eigenschappen. Enkele recente ontwikkelingen zullen worden behandeld.*

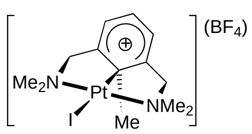


Figure 1. An example of a stable arenonium complex with an σ-bonded Pt^{II} substituent.

Aryl ligand precursors that contain sp^2 N-donor substituents (such as 2-pyridyl) can be cyclometallated at the central C_{aryl}–H bond by complexes of Ru or Os. This has led to the isolation of dinuclear complexes containing terpyridine-type chromophores bridged by a rigid bis-cyclometallating ligand (Figure 2).[13] These compounds contain the metal in a formally +2 or +3 oxidation state and show interesting photoluminescent properties. Cyclometallation has been reported to occur by direct C_{aryl}–H bond activation only.

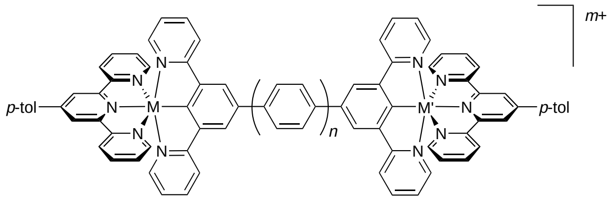
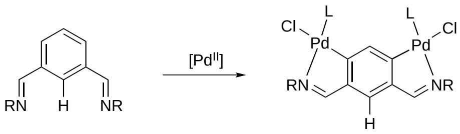


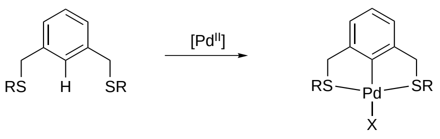
Figure 2. A schematic representation of some bimetallic Ru and Os complexes with an oligophenylene bridging ligand. M, M′ = Ru, Os; n = 0,1,2; m = 2,3,4.

Direct metallation of aryl ligands that contain N-donor atoms in the form of Schiff bases can also be cyclopalladated by an C_{aryl}–H bond cleavage reaction.[14] However, the central C–H bond is not activated [Eq. (5)]. Instead, reactivity is similar to that observed for the corresponding sp^3 N-donor substituted arenes, that is, 4,6-bispalladium(II) aryl complexes are isolated.



(5)

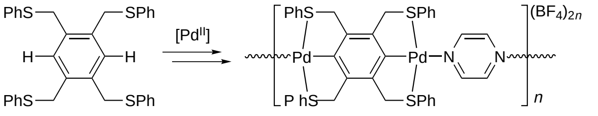
Related chemistry with aromatic compounds containing S-donor atoms has also been investigated. Aryl ligand precursors that contain two *meta*-positioned S-donor substituents can be cyclometallated selectively at the central C_{aryl}–H bond by a number of palladium(II) complexes [Eq. (6)]. Early work by Shaw et al.[15] had suggested that only arenes containing bulky groups at the S-donor atoms could be successfully activated at the central C–H bond. Much later, Pfeffer's group was able to show that $1,3\text{-}(MeSCH_2)_2C_6H_4$ can be cyclopalladated in high yield if an appropriate Pd precursor is used in the presence of one equivalent of acid [Eq. (6)].[16] No



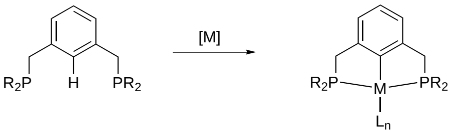
(6)

products of 4,6-bis-cyclopalladation have been observed with these ligands, suggesting that both S-donor groups are coordinated to the metal centre before metallation of the C–H bond.

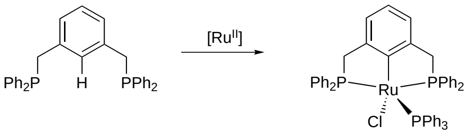
This cyclopalladation chemistry has been successfully applied in the synthesis (by self-assembly) of multinuclear organopalladium(II) spheres[17] and related polymers [Eq. (7)].[18]


(7)

A very large body of work has been devoted to the area of intramolecular metallation of *meta*-substituted aryldiphosphanes. This is an obvious extension of early work on polydentate organophosphorus ligands in which the aryl carbanion replaces a P donor group. Early research in this area was also carried out by Shaw et al.[19] and later by Venanzi and others.[20] They reported that 1,3-aryldiphosphanes with either aliphatic (*t*Bu) or aromatic substituents on the P-donor atoms could be cyclometallated. As expected, activation of the central $C_{aryl}-H$ bond was observed with transition metals from Group 9 and 10 [Eq. (8); M = Rh, Ir, (Ni), Pd, Pt; R = *t*Bu, Ph, *i*Pr]. This work was later expanded to include chiral aryldiphosphanes, benzodiphosphaalkenes and phosphanes containing other groups (e.g., R = B cyclohexyl, pyridinyl and *para*-$H_2NC_6H_4$).[21] All of these ligands can be selectively cyclometallated by various PGM complexes directly at the central C–H bond (vide supra). Recently, Kaska and Jensen have reported various iridium and rhodium complexes of 1,3-aryldiphosphanes that have been successfully applied as dehydrogenation catalysts.[2]


(8)

Recently Jia et al.[22] and independently van Koten and co-workers[23] have detailed the use of $[RuCl_2(PPh_3)_4]$ as a versatile starting material for the cyclometallation of *para*-functionalized arylbis(diphenylphosphanes) [Eq. (9)]. In all these examples, no products of 4,6-dimetallation were observed. This work includes the rare isolation of an intermediate of $C_{aryl}-H$ bond activation in which an apparent three-centre two-electron Ru⋯H⋯C bonding motif is observed [Eq. (10)].[24] This complex is formed by the overall reaction of two equivalents of the aryldiphosphane ligand with $[RuCl_2(PPh_3)_4]$ and replacement of Cl^- by OTf^-.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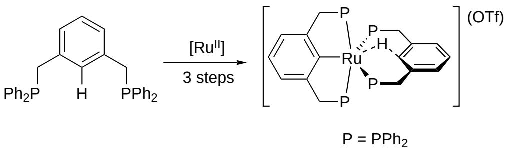
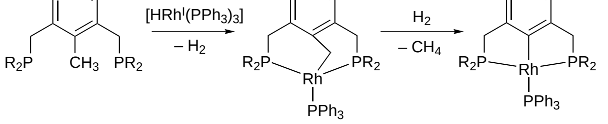
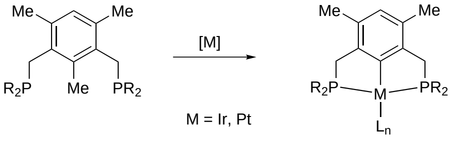

(10)

The desire to improve a number of heterogeneous processes that are used in the refining of petroleum has led to many spectroscopic studies of C–C bond activation by transition metals under homogeneous (solution) conditions. An indirect consequence of this work has been an overall improvement of the synthetic protocols that are used to produce organometallic complexes by C–C bond cleavage. An elegant example of this was illustrated by Milstein and co-workers[25] in the cleavage of the central unstrained $C_{aryl}-CH_3$ bond of the aryldiphosphine $[1,3\text{-}(R_2PCH_2)_2\text{-}2,4,6\text{-}(H_3C)C_6H]$ by rhodium(I) and rhodium(III) compounds [Eq. (11)]. This reaction occurs by initial $C_{alkyl}-H$ bond activation (at 25 °C), followed by an intramolecular $C-CH_2$ bond cleavage reaction.


(11)

This kind of reactivity has been shown in a number of related Pt and Ir systems. These complexes all cyclometallate aryldiphosphanes through activation of the central $C_{aryl}-CH_3$ bond [Eq. (12)].


(12)

The mechanism proposed for this novel C–C bond cleavage involves an arenonium complex with a σ-bonded metal substituent as one of the key intermediates (cf., Figure 1). In our earlier work on related Pt compounds, it has been shown that the central $C_{aryl}-CH_3$ bond of an arenonium complex could be cleaved to afford the corresponding NCN–Pt^{II} (cf., PCP–Pt^{II}, Eq. (12)) species.[12]

In conclusion, it has been demonstrated that $C_{aryl}-R$ bond activation processes can be readily facilitated by a number of platinum group metals to form interesting and catalytically active transition metal complexes. The development of facile syntheses by direct chemoselective (e.g., C–H vs. C–$SiMe_3$) cyclometallations has greatly increased the availability of these useful compounds.

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