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Transcyclometalation, a versatile methodology for multiple metal–carbon bond formation with multisite ligands

Harm P. Dijkstra, Martin Albrecht and Gerard van Koten*

Debye Institute, Department of Metal-Mediated Synthesis, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands. E-mail: g.vankoten@chem.uu.nl

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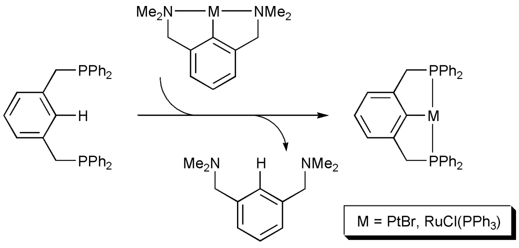
Transcyclometalation has been successfully applied for the multi-platination and -ruthenation of 'cartwheel'-type ligand systems containing six potential metal binding sites, thus providing a method for multiple metal–carbon bond formation *via* C–H bond activation which is superior to established cyclometalation protocols.

The selective making and breaking of (transient) M–C_{aryl} σ-bonds is pivotal to many catalytic cycles,[1] both in bulk chemistry (*e.g.*, catalytic cracking processes) and in fine chemical syntheses (*e.g.*, metal-mediated (cross-)couplings).[2] Additional intramolecular heteroatom coordination, *i.e.* formation of a metallacycle (cyclometalation) often stabilises such M–C bonds and provides an approach to trap important M–C bond containing intermediates and also to influence the activity of the metal centre.[3,4] So far, two different protocols are available for the preparation of cyclometalated complexes: (i) transmetalation, involving main group organometallic complexes (frequently Mg, Li or Sn) and (ii) direct, heteroatom-assisted C–E bond activation (E = predominantly H, C, SiR_3 or halide).[5] Recently, we introduced the transcyclometalation (TCM) reaction as a new additional concept for the generation of cyclometalated transition metal complexes.†[6] In close relation to (organic) transesterification reactions, TCM reactions comprise the substitution of one cyclometalated ligand by another, as exemplified in Scheme 1. We have now applied this concept for the synthesis of nanosize hexametallic species containing metalated PCP sites. These hexametallic architectures have not (yet) been accessible *via* any of the two other standard methods, because of either incomplete metalation and/or the formation of intractable mixtures. Unique features of the TCM reaction are the mild reaction conditions and the easy separation of the TCM product from the arene.

The dodecaphosphine **1**[7] is a polyfunctional 'cartwheel'-type ligand precursor‡ containing six potentially terdentate monoanionic P,C,P′-pincer units (Scheme 2). Initial attempts to directly fully cycloplatinate ligand **1** failed despite using a variety of different metal precursors that previously had been successfully applied for the cycloplatination of analogous single site PCP ligands.[8] Most likely, the local phosphine concentration, which is exceptionally high in **1**, leads to the formation of η²-P,P coordinated platinum centres which are unable to undergo subsequent C–H bond activation. This activation process is anticipated to require transient decoordination of one phosphine ligand in order to generate the electronically and coordinatively unsaturated reactive intermediate.[9] Furthermore, bis(ortho)lithiation of **1** suffered from low selectivity owing to the relatively high acidity of the neighbouring benzylic protons. Consequently, following existing transmetalation protocols did not lead to the formation of **2**.



Scheme 1 The transcyclometalation (TCM) reaction.

In contrast to the difficulties encountered in the latter reactions, treatment of **1** with 6 equivalents of the cycloplatinated complex [PtBr(NCN)] in toluene at reflux for 7 days afforded the hexaplatinum complex **2** (isolated in 30% yield; Scheme 2).§ Purification of **2** (soluble in $CHCl_3$) was achieved by repetitive extraction and precipitation procedures using $CHCl_3$ and Et_2O, respectively. Complete transcyclometalation was unequivocally assessed by multinuclear NMR spectroscopy, and independently by mass spectrometry (MALDI–TOF). For example in the ^1H NMR spectrum, the resonance due to the $ArCH_2P$ protons are characteristically shifted towards lower field upon metal insertion (δ_H 2.88 in **1** and 3.07 in **2**) and no signals due to traces of metal-free PCP units or residual [PtBr(NCN)] were detected. The ^{31}P NMR spectrum is diagnostic and displays a single resonance at 36.1 ppm ($^2J_{PtP}$ 1432 Hz) due to the *trans*-phosphorus nuclei of the PCP ligand sites that are coordinated to platinum. No signals were observed which could point to only partial metalation, which is remarkable and emphasises the scope of the TCM reaction.

The origin for the selectivity and activity of the TCM reaction in comparison with the conventional methods is presumably related to the peculiar mechanistic trajectory of the TCM reaction we documented earlier.[6] The precursor monoaryl [PtBr(NCN)] has (thermodynamically and kinetically) a rigid *trans*-N,N-configuration and therefore forces eventually formed bisaryl platinum intermediates (*i.e.*, [Pt(PCP)(NCN)] type structures) to have a *trans*-C,C-configuration. Most of the frequently used metal precursors, however, do not exclude *per se* the formation of alternative species with the heteroatom donors in mutual *cis*-configuration, which prevents cyclometalation and which is—particularly in the cartwheel compounds as presented here—likely to promote rigid η²-P,P-bidentate *cis*-coordination of adjacent phosphine sites.[10]

The potential of the TCM reaction to create multiple metal–carbon bonds under mild conditions (*e.g.*, in terms of pH, auxiliaries) is further underlined by the reactivity of **1** in the presence of [RuCl(NCN)(PPh_3)] (benzene at reflux temperature). Preliminary investigations showed that the air-sensitive dark green hexaruthenium complex **3** was formed in a similar sequence of TCM reactions (Scheme 2). The NMR spectra of this multimetallic species are uniformly broad, which most likely is due to dynamic processes involving the relative orientation of the PCP aryl planes, which differ because of the five-coordination at the ruthenium centre (Scheme 2 shows only one of the several possible conformations). The ^{31}P NMR spectrum shows two peaks (δ_P 80.8 (m) and 40.7 (m), the multiplicity of the peaks are probably due to different conformers) with chemical shifts in agreement with those found for the monometallic analogue [RuCl(PCP)(PPh_3)] (δ_P 81.3 (t) and 36.5 (d)). For further analysis, **3** was converted into **4**, which contains hexacoordinate ruthenium centres.‡ This was achieved by prolonged reaction (2 d) of a solution of **3** in MeOH with equimolar amounts of 2,2′:6,2″-terpyridine (terpy).[11] This

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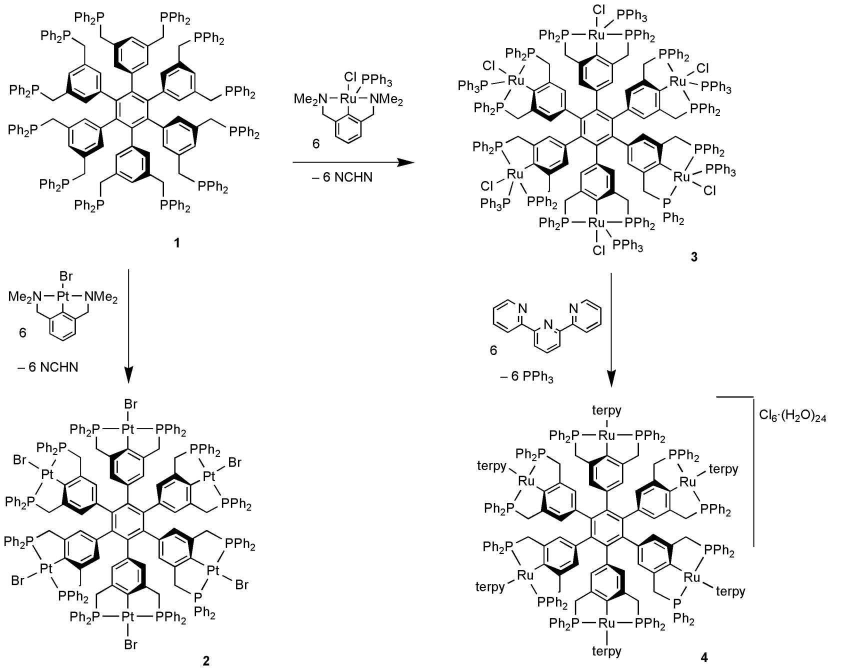

Scheme 2 Synthesis of the hexaarylplatinum(II) complex **2** and the corresponding ruthenium(II) analogues **3** and **4**.

reaction was accompanied by a characteristic colour change from dark green to dark red. The changed geometry around the metal centres in **4** from distorted square-pyramidal to octahedral, had various advantageous consequences: (i) the complex is stable towards air and water, and (ii) the coordination geometry around ruthenium has markedly higher symmetry, thereby reducing the number of potential conformers of **4**. The ^{31}P NMR spectrum now showed a single resonance at δ_P 45.9, which has the value characteristic for a P-centre in a [Ru(PCP)(terpy)]Cl complex.[11] The elemental analysis of **4** revealed a structure with a bruto formula of $C_{288}H_{270}Cl_6N_{18}O_{24}P_{12}Ru_6$, which means that each molecule contains 24 water molecules. This observation was confirmed by ^{1}H NMR spectroscopy, which showed a large peak at δ_H 3.5, which could not only be ascribed to small amounts of water present in the deuterated solvents. By replacing the chlorine counter ions by tetraphenylborane anions, the water molecules could be removed as was shown by ^{1}H NMR spectroscopy. Interestingly this observation suggests that the water molecules in **4** have a distinct orientation, *e.g.*, four water molecules could be bound to each chlorine anion.

Notably, the multimetallic system **3** contains six peripheral metal centres which are catalytically active in selective hydrogen-transfer catalysis with ketones.[12] Structural analysis (X-ray) of related $C_6[(PdCl)\text{-}4\text{-}C_2H_2(CH_2SPh)_2\text{-}3,5)]_6$, showed this species to have a nanosize architecture ($\sim$2 nm),[7] thus suggesting similar dimensions also for **2**, **3** and **4**. Due to the steric rigidity of the organic core, these multisite materials are promising candidates for application as homogeneous catalysts in continuous processes using nanomembrane filtration techniques.

Notes and references

† Ryabov *et. al.*[13] reported the synthesis of cyclopalladated *o*-carboranes following a similar concept, however they did not explore this further.

‡ This term is used for multi-ligand systems containing the central core atoms (benzene) and all metal–carbon bonds in the same plane.

§ An isolated yield of 30% for hexaplatinated complex **2** means at least an 82% yield for each individual metalation step. We also found a considerable amount of fully cycloplatinated (according to ^{31}P NMR) side-products, most probably a mixture of intermediates on the trajectory to **2**, see ref. 6. *Selected analytical data* for **2**: ^{1}H NMR (CDCl$_3$, 200 MHz, SiMe$_4$): δ 7.84–6.47 (m, 132 H, C$_{aryl}$–H), 3.07 (br, 24 H, $^3J_{PtH}$ 28 Hz, ArCH_2P); ^{31}P NMR (CDCl$_3$, 81 MHz, H$_3$PO$_4$): δ 36.1 ($^2J_{PtP}$ 1432 Hz, CH$_2$P); MALDI-TOF (*m*/*z*): 4557.74 (calc. M$^+$: 4557.11), 4478.12 (calc. M$^+$ − Br: 4477.20), 4315.55 (calc. M$^+$ − 3Br: 4317.38).For **3**: ^{1}H NMR (CDCl$_3$, 200 MHz, SiMe$_4$): δ 8.1–6.4 (br m, 222 H, C$_{aryl}$–H), 3.67 (br, 12 H, ArCH_2P), 3.19 (br, 12H, ArCH_2P); ^{31}P NMR (THF-d_8, 81 MHz, H$_3$PO$_4$, 193 K): δ 80.8 (m, PPh$_3$), 40.7 (app. m, CH$_2$P).For **4**: ^{1}H NMR (DMSO-d_6, 300 MHz, SiMe$_4$): δ 9.2–6.0 (br m, 198 H, C$_{aryl}$–H), 3.52–4.40 (br m, 24 H, ArCH_2P); ^{31}P NMR (DMSO-d_6, 81 MHz, H$_3$PO$_4$): δ 45.9 (CH$_2$P). Elemental analysis showed the expected C:N:P ratio: Anal. Calc. for $C_{288}H_{222}Cl_6N_{18}P_{12}Ru_6\cdot 24H_2O$: C, 62.23; H, 4.90; N, 4.54; P, 6.69. Found: C, 62.84; H, 4.56; N, 4.45; P, 6.79%.

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