## Diels-Alder cycloaddition as a new approach toward stable $PC(sp^3)P$ -metalated compounds<sup>†</sup>

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A straightforward synthetic route toward a new family of dibenzobarrelene-based cyclometalated compounds is described.

Pincer-like compounds are now well studied and recognized as efficient catalysts in a variety of chemical transformations, building blocks for construction of advanced materials, as well as components in supramolecular systems.<sup>1</sup> With regard to the carbometalated pincer complexes, the vast majority of reported substances possess an  $sp^2$ -hybridized carbon, while examples of  $C(sp^3)$ -based compounds appear in the literature only occasionally.<sup>2</sup> This imbalance, arguably, originates from a greater thermal and conformational stability of the former compared to the latter. This is especially true of complexes bearing all-aliphatic ligands; in these cases, the carbometalated compounds often coexist in equilibrium with isomeric olefinic or carbenic species due to the facile  $\alpha$ - or  $\beta$ -hydride elimination.<sup>3</sup> On the other hand, available experimental data strongly imply a very interesting and unique reactivity of  $C(sp^3)$ -cyclometalated organometallics due to a stronger donating ability of the  $sp^3$ carbon.<sup>2,4</sup> It is thus obvious that the development of a facile synthetic route toward stable compounds of this type will encourage their utilization in many research areas.

We hypothesized that triptycene-like bidentate ligands lacking easily abstractable hydrogen atoms represent a suitable skeleton for construction of stable  $C(sp^3)$ -based pincer complexes (Scheme 1).<sup>5</sup>

Traditionally, pincer complexes of this type are prepared either by C–H activation (Scheme 1, right) or by oxidative insertion of a coordinated transition metal into the C–X bond of the halogenated spacer (Scheme 1, left). Unfortunately, our previous experience with triptycene-based ligands reveals that the central methine hydrogen is insufficiently acidic to be displaced by a proximate metal center.<sup>6,7</sup> By now, we were able to prepare a single example of very stable but catalytically active iridium(III)  $C(sp^3)$ -metalated compound using this strategy,<sup>8</sup> while other tested metals (Ni–Pt, Rh and Ru) failed to form the desired structure.The second route (oxidative addition) is, apparently, feasible, but synthetically more laborious and therefore may be applied to a limited number of targets.

Therefore we envisioned a conceptually different synthetic approach toward the desired class of compounds which relies

on a one-step transformation of readily available and structurally simple anthracene-based 9-C( $sp^2$ )-metalated complexes<sup>9</sup> into more complex C( $sp^3$ )-metalated ones by means of Diels–Alder cycloaddition as depicted in Scheme 2. Our belief is that successful application of this strategy to specially designed transition metal precursors and dienophiles in a combinatorial manner may result in a diversity-oriented approach toward the family of C( $sp^3$ )-based pincer complexes.

Initially, we tested a reaction between the known and readily available palladacycle  $1^{9a}$  and dimethyl acetylenedicarboxylate as a dienophile.



We were glad to realize that the *organometallic* compound **1** reacts smoothly under thermal conditions resulting in the formation of the [4 + 2] adduct **4** in boiling diethylene glycol diethyl ether (anisole can be used instead) in 71% yield. The choice of solvents appears to be critical for the successful transformation. The formation of **4** was only sluggish in less polar solvents, such as xylene (apparently due to a low solubility of the transition metal precursors), and less efficient in protic solvents, such as ethylene glycol monomethyl ether. In the latter case, we suspect the formation of transesterification by-products, which complicate the final work-up.

Analogous transformations were performed using the known Ni  $(2)^{9a}$  and new Pt (3) C( $sp^{3}$ )-cyclometalated precursors. The expected products **5** and **6** were isolated in 73 and 81% yield, respectively.

It is interesting to note that the difference in <sup>31</sup>P-NMR spectra of the precursors *versus* products is very small in all cases (1–2 ppm shift). However, the change of hybridization at C-9 and C-10 can be clearly detected by <sup>1</sup>H-NMR measurements thanks to a very characteristic highfield chemical shift of



**Scheme 1** Possible synthetic approaches toward  $PC(sp^3)P$ -complexes based on the triptycene spacer.

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Scheme 2 Diels–Alder approach toward  $PC(sp^3)P$ -complexes.

the H-10 signal (from *ca*. 8.3 ppm in **1–3** to *ca*. 5.8 ppm in **4–6**) that takes place over the course of the reaction. Other NMR data also match the proposed structure (see supporting information†).

Despite the unambiguity in identification of the new compounds, the single crystals of **4** and **5** were subjected to X-ray analysis<sup>10</sup> (ORTEP pictures are given in Fig. 1). As expected, unlike in the square planar **1**, the palladium center in  $C(sp^3)$ metalated **4** is strongly distorted from planarity toward a butterfly-like environment. For example, the observed P(1)–Pd–P(2), C(1)–Pd–Cl(1) angles and P(1)–P(2) intramolecular distance between the two phosphorus atoms are 150.43(4)°, 171.86(11)° and 4.427 Å, respectively. As expected, the Pd–Cl bond in **4** is slightly longer than the corresponding bond in the previously reported **1** due to a stronger *trans* influence exerted by the C(*sp*<sup>3</sup>) ligand.<sup>9a</sup> Very similar structural features were observed for the nickel analog **5**.

Thermogravimetric tests showed that the thermal stability of the new compounds is exceptional and in some cases exceeds the stability of  $C(sp^2)$ -metalacycles. For example, the first weight loss detected for **4** takes place at 370 °C and this is 120 °C higher than for the parent **1**. **5** and **6** also demonstrated decomposition points far over 280 °C.

Since very often an extreme stability may indicate chemical inertness, it was important for us to demonstrate at early stages of the study that this is not the case for the new family of compounds. We tested **4** as a promoter in the well-explored Mizoroki–Heck reaction which typically serves as a model reaction for evaluating the catalytic activity of pincer complexes.<sup>11</sup>

We were pleased to find that despite the exceptional thermal stability the new complexes are catalytically active. The following



**Fig. 1** ORTEP drawing (50% probability ellipsoids) of the structures **4** and **5**. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (°) for **4**: Pd1–C1 (2.057(3)), Pd1–C11 (2.3694(9)), Pd1–P1 (2.2908(9)), Pd1–P2 (2.2874(9)), C11–Pd1–C1 (173.14(10)), P1–Pd1–P2 (148.53(3)), C1–Pd1–P1 (96.96(3)). Selected bond lengths (Å) and angles (°) for **5**: Ni1–C1 (1.961(4)), Ni1–C11 (2.2069(12)), Ni1–P1 (2.1872(12)), Ni1–P2 (2.1977(12)), C11–Ni1–C1 (165.57(12)), P1–Ni1–P2 (146.64(5)), C1–Ni1–P1 (86.60(12)).

reaction is driven to completion by only 0.001 mol% of **4** in 12 h which corresponds to at least  $10^5$  TON.



To conclude, we have demonstrated that the unprecedented Diels–Alder reaction of organometallic dienes with organic dienophiles is indeed possible and appears to be a straightforward synthetic route toward dibenzobarrelene-based  $C(sp^3)$ -metalated pincer complexes. More detailed studies on the new family of compounds will follow.

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- 10 Crystallographic data for **4**:  $C_{44}H_{33}ClO_4P_2Pd$ , M = 829.49, orthorhombic, a = 8.3159(5), b = 11.2104(7), c = 38.813(2) Å,

 $U = 3618.4(4) \text{ Å}^3$ , T = 173 K, space group  $P2_12_12_1$ , Z = 4, 40 630 reflections collected, unique 7909 ( $R_{\text{int}} = 0.0515$ ), final *R* indices [ $I > 2\sigma(I)$ ]  $R_1 = 0.0376$ ,  $wR_2 = 0.0818$ . Crystal data for 5:  $C_{48}H_{41}\text{ClNiO}_5P_2$ , M = 853.91, triclinic, a = 10.870(2), b = 14.914(2), c = 17.181(3) Å,  $U = 2538.0(7) \text{ Å}^3$ , T = 173 K, space group  $P\overline{I}$ , Z = 2, 26 275 reflections collected, unique 9920 ( $R_{\text{int}} = 0.0676$ ), final *R* indices [ $I > 2\sigma(I)$ ]  $R_1 = 0.0802$ ,  $wR_2 = 0.2254$ . CCDC 699997 and CCDC 699996 contain the supplementary crystallographic data for this paper (**4** and **5**, respectively).

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