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Citation for final published version:

Chapman, Andy M., Flynn, Stephanie R. and Wass, Duncan F. 2016. Unexpected formation of early late heterobimetallic complexes from transition metal frustrated Lewis pairs. *Inorganic Chemistry* 55 (3) , pp. 1017-1021. 10.1021/acs.inorgchem.5b01424

Publishers page: <http://dx.doi.org/10.1021/acs.inorgchem.5b01424>

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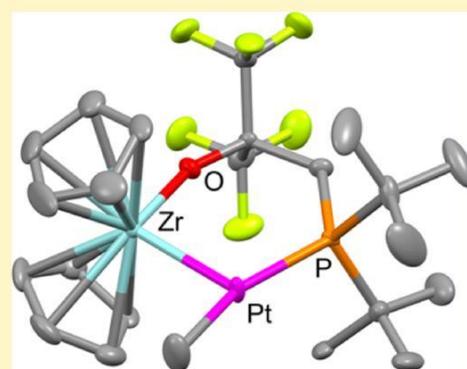
Unexpected Formation of Early Late Heterobimetallic Complexes from Transition Metal Frustrated Lewis Pairs

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* Supporting Information

ABSTRACT: Reaction of transition metal “frustrated” Lewis pair compounds of the type $[\text{Cp}_2\text{Zr}(\text{Me})(\text{OC}(\text{CF}_3)_2\text{CH}_2\text{P}^t\text{Bu}_2)]$ with the low valent platinum species $[\text{Pt}(\text{norbormene})_3]$ leads to the unexpected formation of a heterobimetallic species $[\text{Cp}_2\text{Zr}\{\text{Pt}(\text{Me})\}(\text{OC}(\text{CF}_3)_2\text{CH}_2\text{P}^t\text{Bu}_2)]$. Single crystal X-ray analysis reveals an unusual T-shaped geometry at the platinum center, with a relevant C–Pt–P angle of $163.3(3)^\circ$. Treatment of this compound with PMe_3 yields $[\text{Pt}(\text{PMe}_3)_4]$ and regenerates the zirconium precursor. Treatment with $[(\text{Et}_2\text{O})_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ protonates off the methyl ligand to give an ether adduct at platinum. Analogous observations are made with titanium–platinum species. We propose the chemistry is best rationalized as a formal insertion of $\text{Pt}(0)$ into a Zr–C or Ti–Cl bond.



INTRODUCTION

Frustrated Lewis pair (FLP) chemistry, in which Lewis acid–base pairs act cooperatively to activate small molecules such as hydrogen and CO_2 , is one of the most exciting recent developments in main group chemistry, not least because of the promise of catalysis with such FLPs.¹ We² and others³ have extended this chemistry to transition metal systems, replacing the main group Lewis acid with an electrophilic group 4 fragment to give highly reactive FLPs based on metallocene phosphinoaryloxy complexes. Recently, we have also demonstrated that the Lewis basic component of FLPs can be a low valent late transition metal complex with a combination of $\text{B}(\text{C}_6\text{F}_5)_3$ and platinum(0) diphosphine complexes exhibiting FLP-type reactivity as well as new reaction pathways.⁴ With examples of transition metals replacing either the main group Lewis acidic or Lewis basic component of an FLP now established, we were intrigued by the possibility of having both the Lewis acidic and basic functions as transition metals.⁵ This possibility is, of course, reminiscent of early late heterobimetallic complexes, which have been studied for many years.^{6–8} It is particularly intriguing that some of these complexes have already been reported to activate small molecules such as CO_2 , albeit the analogy to FLPs has not been drawn.^{9,10} Our preliminary investigation into the preparation of an all-transition metal FLP based on extending the group 4 metallocene phosphinoaryloxy scaffold has led to surprising results, which we report here.

RESULTS AND DISCUSSION

We have already reported the synthesis of the neutral alkoxy/alkyl-metallocene complex 1 as a precursor to our cationic transition metal FLP complexes.^{2d} We envisaged that the pendant phosphine moiety in these neutral precursors may be

used to tether an electron-rich transition metal in close proximity to the metallocene so that abstraction or protonation of the methyl ligand by standard methods would furnish the target complexes (Figure 1).

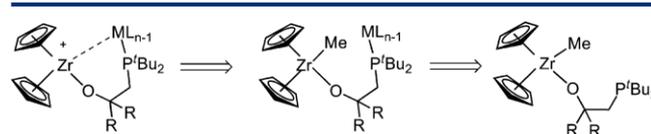


Figure 1. Retrosynthesis of proposed heterobimetallic cation. Anion (omitted for clarity) = $[\text{B}(\text{C}_6\text{F}_5)_4]$. M = group 10 metal, L = generic ligand, and R = Me or CF_3 .

Our initial focus was to investigate $\text{Pt}(0)$ as the electron-rich transition metal component in the target systems, choosing to work with $[\text{Pt}(\text{nb})_3]$ (nb = norbornene) due to its relative ease of handling and precedent for forming monophosphine complexes of the type $[(\text{R}_3\text{P})\text{Pt}(\text{nb})_2]$ (R = Ph, Cy).¹¹ However, treatment of the neutral alkoxy/alkyl-precursor 1 with $[\text{Pt}(\text{nb})_3]$ does not yield the anticipated monophosphine complex. Instead, a rare T-shaped complex (2, Figure 2) is isolated in almost quantitative yield (quantitative by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy) that arises from insertion of a $\text{Pt}(0)$ fragment into the Zr–C bond. No other species were detected during the course of the reaction by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy.

Compound 2 was isolated in high yield as a yellow crystalline solid by precipitation from hexane at low temperature. The $^{195}\text{Pt}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR resonances of 2 occur at -3365

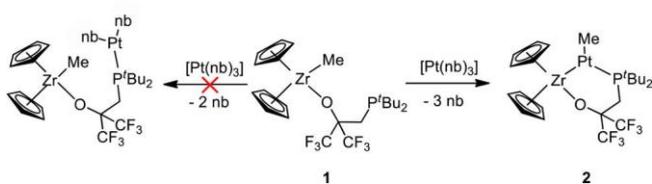


Figure 2. Synthesis of compound 2. Reagents and conditions: one eq [Pt(nb)₃], PhH, 25 °C, 8 h.; nb = norbornene.

and 77 ppm (¹J_{Pt} = 2172 Hz, c.f 3320 Hz in [(ZrCl₄)Pt(PCy₃)₂]).¹² The solid state structure of 2 clearly shows the T-shaped geometry of the complex with a C7–Pt1–P6 angle of 163.3(3)°; there are very few examples of Pt complexes with this geometry.¹³ Note that while the number of well characterized three-coordinate Pt(II) complexes is very low, the number of “masked” structures (whereby the vacant site is filled by a coordinated anion, solvent molecule, or agnostic interactions) is greater and has important implications as catalytically relevant intermediates.¹⁴ The presence of a supported Zr–Pt bond is also observed (Figure 3); although

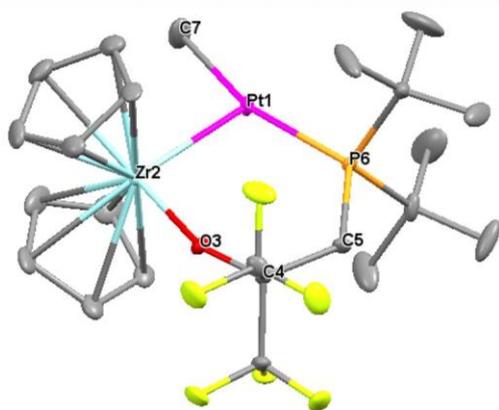


Figure 3. Crystal structure of 2. Displacement ellipsoids are shown at 30% probability, and hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Zr2–O3 1.991(5), O3–C4 1.351(9), P6–Pt1 2.304(2), Pt1–Zr2 2.5343(7), Pt1–C7 2.08(1), Cp–Zr2 2.246, 2.262 Angles (deg): Zr2–O3–C4 158.9(4), Pt1–Zr2–O3 96.6(1), Zr2–Pt1–P6 100.38(4), Zr2–Pt1–C7 96.3(3), C7–Pt1–P6 163.3(3), and Cp–Zr2–Cp = 126.87.

there is only one other example of such a bond and thus very little basis for comparison, the Zr–Pt bond in 2 (2.5343(7) Å) is remarkably similar to that in the unsupported Zr–Pt species [(ZrCl₄)Pt(PCy₃)₂] at 2.5258(6) Å.¹² Solid samples of 2 appeared to be stable for several weeks in the solid state under an inert atmosphere, but benzene solutions of 2 decompose slowly to unidentified products over the course of several days with the concomitant precipitation of dark solid, presumably platinum metal. Attempts to obtain satisfactory elemental analysis of 2 have been frustrated by obtaining low values, which are consistent with around 0.1% of a persistent platinum metal contaminant.

To further probe the unusual structure of 2, calculations at the density functional level of theory were performed. Geometry optimization of the crystal structure, taking into account dispersion and solvent effects, showed little variation, suggesting the unusual Zr–Pt bond to be favorable. Table 1 provides a comparison of key bond lengths and angles between the crystal structure and computed structure.

To verify the stability of this structure further, geometry optimizations were also performed on a structure in which the Zr–Pt interaction is removed, and groups rotated away from one another. The resulting energy difference in the two optimized structures is over 78 kcal/mol^{−1} in favor of the bonded structure. From analysis of the structures, there are no agostic interactions between the *tert*-butyl groups and platinum, evidence which is supported by NMR spectroscopy, indicating this is a “true” T-shaped Pt complex.

Figure 4 shows the frontier molecular orbitals (HOMO/LUMO) for the optimized crystal structure. It is clear that the

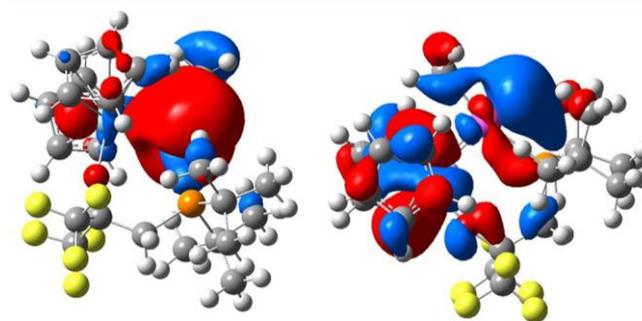


Figure 4. Surfaces of HOMO and LUMO frontier molecular orbitals at the M06/6-31G* level of theory. Highest occupied molecular orbital (left) and lowest unoccupied molecular orbital (right).

HOMO is localized primarily on the Pt center with smaller amounts of electron density on the methyl group and Zr. Again, the LUMO is centrally located on the platinum and zirconium, seemingly depicting the σ^* MO, with the presence of a large orbital on the Pt that is sterically unhindered and would be a favorable position for nucleophilic attack. Preliminary experiments in this regard have revealed that the Zr–Pt bond is surprisingly stable toward potential substrates. Figure 5 depicts the corresponding Pt–Zr σ MO. Also, 2 reacts cleanly with an excess of PMe₃, to afford known [Pt(PMe₃)₄]¹⁵ and 1 (Figure 6).

Although not the desired product of the reaction, we were keen to see if 2 would still serve as a viable precursor to the expectantly more reactive cationic species. With a view to accessing an unsaturated species, methyl abstraction from 2 using [CPh₃][B(C₆F₅)₄] or oxidative cleavage using [(C₅H₄Me)₂Fe][B(C₆F₅)₄] in noncoordinating (chlorobenzene, fluorobenzene) or weak donor solvents (pentafluoropyridine) was attempted. However, in all cases, this led to the formation of intractable mixtures of products. Using [(Et₂O)₂H][B(C₆F₅)₄]¹⁶ as both a source of acid for protonolysis and stabilizing ether ligand, a much cleaner

Table 1. Comparison of Bond Lengths in Crystal Structure and Optimized Geometry

	Zr–Pt/Å	Pt–C–H ₃ /Å	P–Pt/Å	Zr–O/Å	Zr–Cp*/Å	Pt–Zr–O/deg	Zr–Pt–P/deg
crystal	2.5343(7)	2.08(1)	2.304(2)	1.991(5)	2.53	96.6(1)	100.38(4)
DFT	2.627	2.093	2.386	2.018	2.54	92.85	99.81

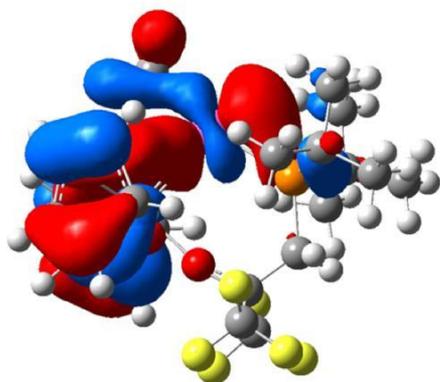


Figure 5. Surface of HOMO(-6) frontier molecular orbital at the M06/6-31G* level of theory.

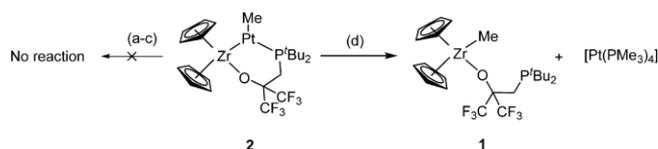


Figure 6. Reactivity of 2 toward potential ligands. Reagents and conditions: (a) 2 bar H₂, PhH, 1–24 h, 25 °C; (b) 2 bar ¹³CO₂, PhH, 1–24 h, 25 °C; (c) 2 bar ethene, PhH, 1–24 h, 25 °C; (d) approximately 10 eq. PMe₃, PhH, 5 min, 25 °C.

reaction was observed at NMR scale. Upon mixing, a distinct color change from yellow to orange was observed and the formation of one equivalent of MeH (detected by ¹H NMR spectroscopy, δ , 0.23 ppm).¹⁷ The presence of a cationic complex is proposed from definitive changes in the ¹H and ³¹P{¹H} NMR spectral data (loss of the Pt-Me signal and gain of residual ether in ¹H and shift of the ³¹P resonance to 66.1 ppm). The expected oxidation of the Pt center is consistent with an increase in the ¹J_{Pt} (from 2171 to 5933 Hz in 3). Noteworthy is that only one set of diethyl ether signals are observed. This could be explained by either rapid exchange of the ether ligands in 3 or symmetrical coordination of both diethyl ethers (Figure 7). The ¹H NMR spectrum of 3 gives integration of the relevant signals, which is intermediate between one and two ligands. DFT studies reveal the likelihood of a single diethyl ether moiety coordinating. Indeed, the geometry optimization with two ether moieties failed to converge, with intermediary geometries giving a result where one ether is coordinated relatively close (2.816 Å) the other at a large distance (4.250 Å).

To explore the generality of this chemistry to the other group 4 elements, the Ti complex 5 was synthesized by reaction of titanocene 4 with [Pt(nb)₃] in chlorobenzene (Figure 8). Compound 5 was isolated in quantitative yield as a highly

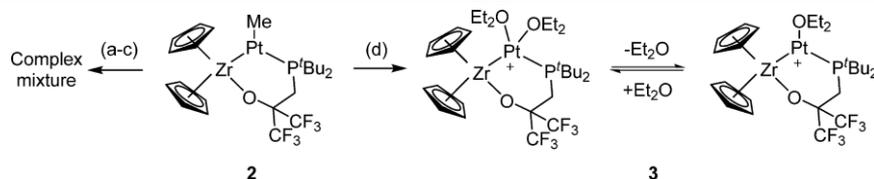


Figure 7. Attempted synthesis of the corresponding cationic complex of 3 by methyl abstraction (left) and successful synthesis via protonolysis (right). Reagents and conditions: (a) 0.98 eq. [CPh₃][B(C₆F₅)₄], PhCl, 25 °C, 10 min; (b) 0.98 eq. [CPh₃][B(C₆F₅)₄], pentafluoropyridine, 25 °C, 10 min; (c) 0.98 eq. [(C₅H₄Me)₂Fe][B(C₆F₅)₄], PhCl, 25 °C, 8 h; (d) 0.98 eq. [(Et₂O)₂H][B(C₆F₅)₄], DCM-d₂, 25 °C, 8 h.

Figure 8. Synthesis of compound 5. Reagents and conditions: 1.01 eq. [Pt(nb)₃], PhCl, 25 °C, 12 h; nb = norbornene.

insoluble brown crystalline solid that precipitated over 12 h. The ³¹P{¹H} NMR resonance of 5 occurs at 39.1 ppm (¹J_{Pt} = 5208 Hz, c.f. 4805 Hz of the bridging ligand in [CpTi(μ-CH)PPh₂Pt(O(PhC CH)PPh₂)]), supporting formation of the Pt-P bond and by inference a Ti-Pt bond. While NMR spectroscopic data and elemental analysis supports the formation of 5, efforts to grow crystals suitable for X-ray crystallography have been unsuccessful to date. In contrast to 2, complex 5 appears remarkably stable in the solution phase and indeed even in air over the course of weeks. Few examples of complexes containing a Ti-Pt interaction exist^{18,19} and, to our knowledge, none containing the proposed geometry.

CONCLUSION

We have discovered that the reaction of a metallocene phosphinoaryloxo transition metal-based frustrated Lewis pair with [Pt(nb)₃] leads to the unexpected formation of a T-shaped Pt complex with a supported Zr-Pt bond. This type of complex is rare but seen through the prism of recent results in Z-type ligands can be rationalized in terms of the Zr center acting as a transition metal Z-type ligand, rather than the more common boron-based fragments. In this way, these results also strengthen the analogy between our complexes and main group FLPs, demonstrating that main group Lewis acids and electrophilic transition metal complexes can be interchanged in this chemistry.

EXPERIMENTAL SECTION

Unless otherwise stated, all manipulations were carried out under an inert atmosphere of argon using standard Schlenk line and glovebox (M-Braun, O₂ < 0.1 ppm, H₂O < 0.1 ppm) techniques, and all glassware was oven-dried (200 °C) overnight and allowed to cool under vacuum prior to use. Commercially available PMe₃ was purchased from Strem and used as received. Nonstandard reagents were prepared according to the literature and referenced where appropriate. Solvents were purified and predried using an Anhydrous Engineering column purification system and then vacuum transferred from the appropriate drying agent (K/benzophenone for aromatics and ethers; CaH₂ for hydrocarbons and chlorinated solvents) prior to use. NMR spectra were recorded using a Varian 500 spectrometer at (using the appropriate deuterated solvent, purchased from Cambridge Isotope Laboratories or Sigma-Aldrich and purified by vacuum transfer from the appropriate desiccant) and referenced to an internal standard (residual solvent signal for ¹H, 85% H₃PO₄ for ³¹P, and FCCL₃ for ¹⁹F

NMR. Spectra of air and moisture sensitive compounds were recorded using resealable J-Youngs tap NMR tubes. Microanalysis was carried out by the Microanalytical Laboratory, University of Bristol, using a Carlo Erba spectrometer.

Synthesis of Compound 2. Compound 1^{2d} (116.8 mg, 0.205 mmol) and [Pt(nb)]₃ (463.1 mg, 0.205 mmol) were weighed into a small vial and dissolved in benzene (3 mL). The resulting bright yellow solution was allowed to stand for ca. 20 h and then filtered through a glass fiber plug into a clean Schlenk flask. The flask was sealed, removed, and connected to a Schlenk line where the solvent was removed. The resulting yellow powder was left under high vacuum overnight and then returned to the glovebox and isolated. Large yellow block-shaped crystals were grown by slow evaporation of a benzene/hexane (1:1) solution at room temperature. Yield: 337 mg, 0.60 mmol, 98%. ¹H NMR (benzene-d₆): δ 6.24 (s, 10H, C₅H₅), 1.35 (d, ²J_{HP} = 10.1 Hz, 2H, CH₂), 0.96 (d, ³J_{HP} = 13.2 Hz, 18H, C(CH₃)₃), 0.72 (d, ³J_{HP} = 7.9 Hz, 3H, PtCH₃). ¹³C{¹H} NMR (benzene-d₆): δ 125.2, (q, ¹J_{CF} = 292.7 Hz, C(CF₃)₂), 114.5 (s, C₅H₅), 85.9 (m, C(CF₃)₂), 37.9 (d, ¹J_{CP} = 21.8 Hz, C(CH₃)₂), 31.2 (d, ²J_{CP} = 5.5 Hz, C(CH₃)₂), 12.5 (d, ²J_{CP} = 18.7 Hz, CH₂), 9.5 (d, ²J_{CP} = 71.6 Hz, 3H, PtCH₃). ³¹P{¹H} NMR (benzene-d₆): δ 77.5 (s, ¹J_{PPt} = 2171.8 Hz). ¹⁹F NMR (benzene-d₆): δ -75.7 (s). Elem. Anal. Calcd (%): C 43.04, H 5.03. Found (%): C 42.06, H 4.90.

Reaction of Compound 2 with PMe₃. An NMR tube was charged with Compound 2 (15.1 mg, 0.02 mmol) and benzene-d₆ (0.7 mL). To this, an excess of PMe₃ (ca. 2 drops) was added in one portion. After sealing the tube and shaking, the bright yellow color attributed to 2 was immediately bleached, acquiring the relevant NMR spectra in ca. 5 min. Later revealed 100% conversion to 1 (³¹P{¹H}, ¹⁹F, and ¹H NMR spectroscopy)^{2d} and [Pt(PMe₃)₄] (³¹P{¹H} spectroscopy).¹⁵

Synthesis of [H(OEt)₂][B(C₆F₅)₄]. Modified from a literature procedure,¹⁶ bromopentafluorobenzene (1.99 mL, 16 mmol) was dissolved in hexane (75 mL) and cooled to -78 °C. n-BuLi (1.6 M in hexanes, 10 mL, 16 mmol) was added dropwise, and the solution was stirred for 1.5 h. Caution! Note that the temperature must be kept below -50 °C as lithium pentafluorobenzene reagents are known to be explosive above this temperature. Boron trichloride (1 M in hexanes, 4 mL, 4 mmol) was added dropwise. The reaction mixture was allowed to reach ambient temperature and stirred overnight. The solvent was removed in vacuo, and the solid redissolved in diethyl ether, filtered, and cooled to -30 °C. HCl (2 M in diethyl ether, 8 mL, 16 mmol) was added, and the solution stirred for 4 h. The reaction mixture was warmed to room temperature, filtered, and the solvent removed in vacuo. The remaining residue was dissolved in dichloromethane and filtered through Celite to remove any remaining lithium chloride. The solvent was removed in vacuo, and the resulting white powder recrystallized from diethyl ether at -78 °C yielding large white crystals (2.39 g, 2.88 mmol, 72%). ¹H NMR (300 MHz, DCM-d₂): δ 16.49 (s, 1H, H(OEt)₂), 3.95 (8H, q, ³J_{HH} = 7.01 Hz, CH₃CH₂O), 1.35 (12H, ³J_{HH} = 7.05 Hz, CH₃CH₂O). All NMR data matches those in the literature.¹⁶

Reaction of Compound 2 with [(Et₂O)₂H][B(C₆F₅)₄]. Compound 2 (116.8 mg, 0.205 mmol) and [(Et₂O)₂H][B(C₆F₅)₄]¹⁶ (463.1 mg, 0.205 mmol) were each weighed into small vials and dissolved in DCM-d₂ (0.5 mL each). The solution of [(Et₂O)₂H][B(C₆F₅)₄] was subsequently added dropwise with a microsyringe with rapid stirring. Immediate gas evolution and a darkening of the yellow of 2 to orange was observed. The solution as transferred to an NMR tube, and the relevant NMR spectra acquired. Crystallization of the sample was attempted by layering solution with hexane in the NMR tube; however, after standing overnight, a deep red oil had formed. Decanting the solvents, drying briefly under vacuum, and redissolving this oil in DCM-d₂ gave a dark red solution. However, reacquisition of the NMR spectra revealed the presence of multiple species and no residual signals attributable to 3. ¹H NMR (dichloromethane-d₂): δ 6.82 (s, 10H, C₅H₅), 3.88 (q), 2.33 (d, ²J_{HP} = 10.2 Hz, 2H, CH₂), 1.67 (t), 1.46 (d, ³J_{HP} = 15.0 Hz, 18H, C(CH₃)₃). ³¹P{¹H} NMR (dichloromethane-d₂): δ 66.1 (s, ¹J_{PPt} = 5933.2 Hz). ¹⁹F NMR (dichloromethane-d₂): δ -77.7 (s)

Synthesis of Compound 5. Compound 4^{2d} (45.6 mg, 0.101 mmol) and [Pt(nb)]₃ (47.8 mg, 0.103 mmol) were weighed into a small vial and dissolved in chlorobenzene (1 mL). The resulting dark brown solution was allowed to stand for ca. 20 h leading to precipitation of a dark red/brown microcrystalline solid. Following filtration, the resulting brown crystals were washed with portions of toluene and dried under vacuum. Yield: 62.1 mg, 0.096 mmol, 95%. ¹H NMR (Chlorobenzene-d₅): δ 7.48 (dt, J = 6.98, 1.44 Jz, 1H, H₆), 7.26 (tm, J = 7.69, 1H, H₄), 6.80 (tm, J = 7.48, 1H, H₅), 6.67 (s, 10H, C₅H₅), 6.43 (m, 1H, H₃), 1.51 (d, ³J_{HP} = 13.9 Hz, 18H, P(tBu)₂). ¹³C{¹H} NMR (Chlorobenzene-d₅): δ 173.8 (d, ²J_{CP} = 8.31, C1), 132.7 (s, C6), 131.8 (s, C4), 118.9 (d, J_{CP} = 4.5 Hz, C5), 118.4 (d, ¹J_{CP} = 49.6 Hz, C2), 117.2 (d, J_{CP} = 6.75 Hz, C3), 112.7 (s, C₅H₅), 38.7 (d, ¹J_{CP} = 29.78 Hz, C(CH₃)₂), 31.0 (d, ²J_{CP} = 5.04 Hz, C(CH₃)₂). ³¹P{¹H} NMR (Chlorobenzene-d₅): δ 39.1 (s, ¹J_{PPt} = 5189.1 Hz). Elem. Anal. Calcd (%): C 44.56, H 5.14. Found (%): C 44.10, H 4.92.

CALCULATIONS

All calculations were carried out using the Jaguar²⁰ and GAUSSIAN (version GAUSSIAN09)²¹ software packages. Geometry optimizations were carried out at the density functional level of theory, using the dispersion corrected functional M06 starting from the crystal structure coordinates.²² For all main group elements (C, H, O, P, F), the split-valence double- ζ polarized basis set 6-31G* was employed, whereas for the platinum and zirconium atoms, the Stuttgart/Dresden SDD basis set with an effective core potential was utilized.²³ To investigate the binding of diethyl ether molecules (3), geometry optimization on the relevant structures was performed as above.

The solvent effect during the geometry optimization of 2 was evaluated using the polarizable continuum model (PCM). The solvent employed in this calculation was benzene. The solvent effect for optimization of coordinated ether molecules was also evaluated, this time employing dichloromethane.

ASSOCIATED CONTENT

* Supporting Information

XYZ coordinates of optimized geometries. (PDF)
Crystallographic data in cif file format for compound 2. (CIF)

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Notes

The authors declare no competing financial interest.

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