Activation of P_5R_5 (R = Ph, Et) by a Rh-β-diketiminate complex†

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(NacNac)Rh(C_8H_{14})(N_2) reacts with P_5R_5 to give complexes of formula (NacNac)Rh(P_5R_5) (R = Ph, Et); in the former species inversion of a P atom of P_5Ph_5 allows coordination to a Rh(I) centre, whereas in the later species a P–P bond undergoes oxidative addition to give a formally Rh(III) species.

While the impact of organometallic chemistry and catalysis on organic chemistry has been recognized with several recent Nobel prizes, the extension of the concepts of organometallic chemistry to main group synthesis and materials chemistry is only beginning to draw attention. The approach in the area dubbed "inorganometallics"[1] logically begins with the demonstration of stoichiometric reactivity of transition metal complexes with main group species. Subsequent efforts target stoichiometric and catalytic transformations to main group derivatives. One subset that has been of longstanding interest to our group are inorganometallic avenues to P-based compounds. To this end, we[2–6] and others[7–10] have explored a variety of systems that effect P–H bond activation and demonstrated that the resulting species have a rich chemistry. Based on those findings of stoichiometric reactions, catalysts for dehydrocoupling of phosphines to give diphosphines, oligophosphines or the heterodehydrocoupling of phosphines and silanes to give silylphosphines have been developed.[8,11–13]

A lesser explored alternative to P-based compounds involves the activation of P–P bonds. Indeed, the activation of P–P bonds by transition metal species has previously drawn only limited attention. Recently we showed that a (NacNac)Rh-based catalyst can activate the P–P bond of simple diphosphines (P_2R_4) for either hydrogenation and hydrosilylation.[13] Activation of a P–P bond in an oligophosphine offers a potential route to unique poly-P-containing species. However, oligophosphines have a propensity for fragmentation. For example, while Ang and coworkers demonstrated the ability of P_5R_5 oligophosphines to coordinate to both mono-, bi- and trimetallic metal-carbonyl species,[14] fragmentation of the oligophosphine was observed in some cases. Similarly, in 2006 we reported that P_5R_5 reacts with low valent Fe β-diketiminates resulting in fragmentation of P_5R_5 affording $Fe_2(P_2Ph_2)$ derivatives.[15] In this paper we report the first evidence of activation of P–P bonds in oligophosphines, without such fragmentation. This gentle activation is accomplished by reaction of P_5R_5 with the β-diketiminate-complex Rh(NacNac)(C_8H_{14})N_2 **1**.[16]

Stoichiometric reaction of P_5Ph_5 with **1** results in the formation of a new species **2**, subsequently isolated in 73% yield.§ The ^{1}H NMR data for **2** are consistent with 1 : 1 ratio of the NacNac ligand and P_5Ph_5. Moreover, the ^{1}H NMR spectrum of **2** reveals four signals attributable to four inequivalent isopropyl methine protons. These data clearly reflect a high degree of molecular dissymmetry. The $^{31}P\{^1H\}$ NMR spectrum of **2** is a remarkably well resolved, yet complex pattern exhibiting five sets of resonances ranging from 55 to −15 ppm (Fig. 1), consistent with the presence of five distinct P environments. Use of ^{31}P–^{31}P COSY NMR spectral data revealed the couplings of each of the P atoms to other P nuclei as well as Rh with coupling constants ranging from 2–365 Hz. The extracted coupling constants were employed to simulate the first-order ABCDEX $^{31}P\{^1H\}$ NMR spectrum. Although these data clearly are consistent with an unsymmetrical complex, the precise nature of **2** could not be gleaned from these data, thus necessitating an X-Ray crystallographic study.¶

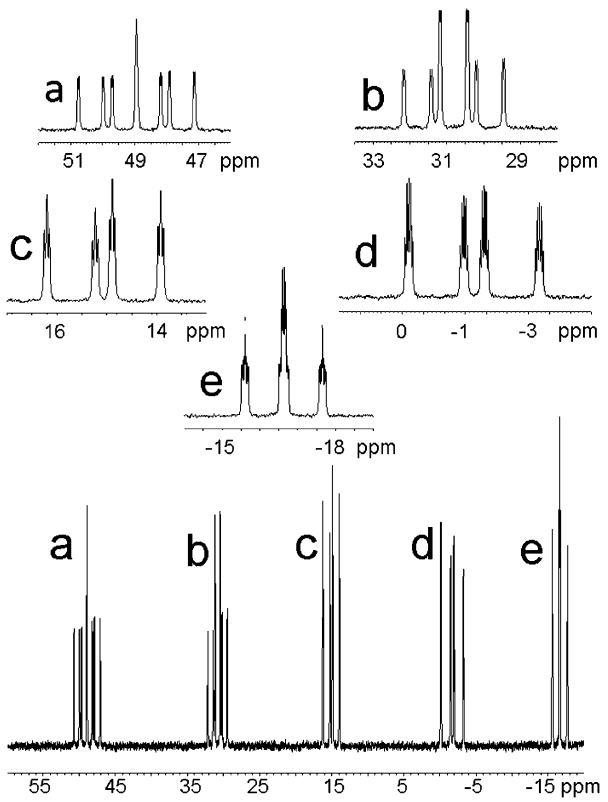

Fig. 1 $^{31}P\{^1H\}$ NMR spectrum of **2**. The full spectrum is shown together with individual magnifications of the resonances a–e.

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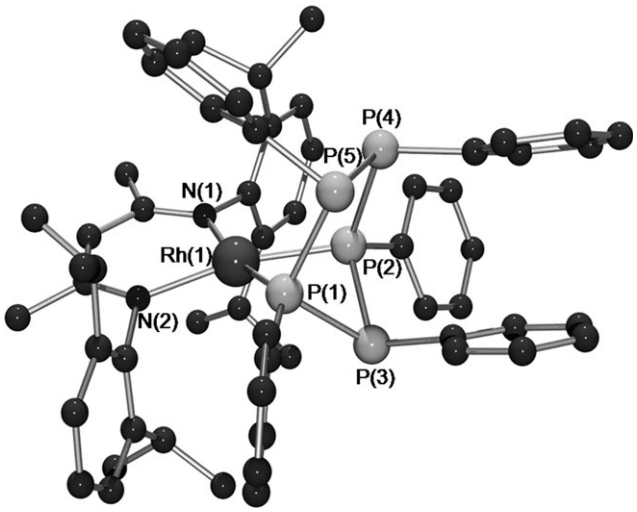
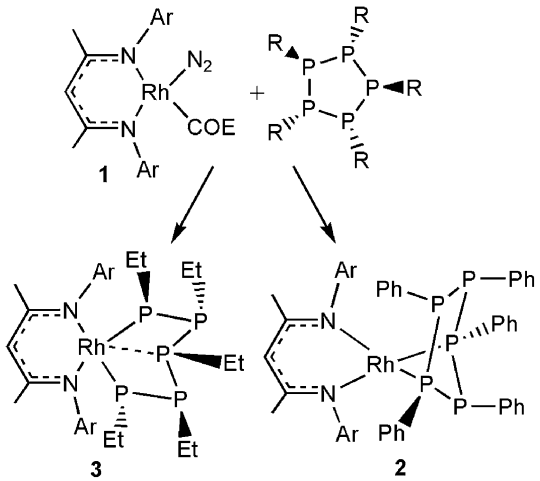


Fig. 2 POV-Ray drawing of **2**, hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Rh–P(1) 2.2488(12), Rh–P(2) 2.2739(12), Rh–N(2) 2.079(3), Rh–N(1) 2.105(4), P(1)–P(3) 2.1791(16), P(1)–P(5) 2.2554(17), P(2)–P(3) 2.2088(17), P(2)–P(4) 2.2452(17), P(4)–P(5) 2.2160(18); N(2)–Rh–N(1) 89.99(14), N(2)–Rh–P(1) 98.58(10), N(1)–Rh–P(1) 168.65(11), N(2)–Rh–P(2) 166.80(10), N(1)–Rh–P(2) 100.91(11), P(3)–P(1)–Rh(1) 93.39(6), Rh(1)–P(1)–P(5) 110.23(6), P(1)–Rh–P(2) 71.69(4), P(3)–P(2)–Rh(1) 91.92(5), P(4)–P(2)–Rh(1) 108.21(6), P(3)–P(1)–P(5) 102.32(7), P(3)–P(2)–P(4) 106.99(7), P(1)–P(3)–P(2) 74.26(6), P(5)–P(4)–P(2) 94.17(6), P(4)–P(5)–P(1) 96.65(6).

Crystals of **2** (Fig. 2) provided confirmation of the general formulation postulated above and revealed that **2** is a pseudo-square planar Rh(I) complex in which the Rh is η^2-coordinated to NacNac and an intact P_5Ph_5 ring. The Rh–N distances were found to be 2.079(3) and 2.105(4) Å, while the N–Rh–N angle is 89.99(14)°. The P_5-ring is bound to Rh in a 1,3 fashion with two of the five P nuclei are above the Rh coordination plane while only one P atom is below. The Rh–P distances were found to be 2.2488(12) and 2.2739(12) Å, respectively, reflecting the inequivalence of the two sides of the coordination plane that is a result of the orientation of the Ph rings on the P atoms. Of the two P atoms above the coordination plane, P(5) has a Ph ring oriented toward the Rh, while the Ph ring on P(4) is oriented away. The P–P bonds were observed in the range 2.1791(16) to 2.2554(17) Å with slightly longer bond P–P lengths in the RhP_4 ring than in the RhP_3 ring presumably reflecting ring strain as evidenced by the acute P(1)–P(3)–P(2) angle of 74.26(6)°.

At first glance this species **2** appears to be simply a result of the coordination of P_5Ph_5 to the Rh centre *via* displacement of the cyclooctene and N_2. However, this is not the case. X-Ray crystallography as well as NMR studies have previously established that the phenyl rings about P_5Ph_5 are oriented in alternating fashion thus minimizing steric conflict.[17] This resulting "down-up-down-up-up" pattern about the ring stands in contrast to the arrangement of the phenyl rings in (**2**) where one phenyl group is oriented towards and the other four are directed away from the metal centre (Scheme 1). In considering the mechanism of formation, it is noted that the barrier to P-inversion for cyclic polyphosphines[14,17,18] has been observed to be substantially less than that of a trialkyl or triarylphosphines. In the present case, oxidative addition of P–P bonds to Rh affording a transient



Scheme 1 Reactions of (**1**) and P_5R_5 (R = Ph, Et).

Rh(III) species must also be considered. Presumably the observed geometry reflects the thermodynamically favored orientation that minimizes steric conflicts between the phenyl substituents and the NacNac ligand on Rh (Fig. 2).

The corresponding reaction of **1** with P_5Et_5 proceeds slowly to give a new species **3** in quantitative yield by ^{31}P NMR spectroscopy although the isolated yield was 43%.‖ Monitoring the reaction by $^{31}P\{^1H\}$ NMR spectroscopy revealed the slow conversion to **3**. Initially the reaction mixture showed a complex ^{31}P resonance pattern that simplified over the course of two weeks to give a spectrum of five multiplets in the range between −110 to 80 ppm. ^1H NMR data were also consistent with the presence of NacNac and P_5Et_5 fragments in a 1 : 1 ratio, as well as with five distinct ethyl group environments.

An X-Ray crystallographic study of **3** (Fig. 3) confirmed the presence of a compound with the empirical formula (NacNac)Rh(P_5Et_5).** In contrast to **2**, the P_5-unit is not cyclic as Rh has oxidatively added one of the P–P bonds resulting in a *cis* orientation of the resulting phosphide units (P(1), P(5)) with Rh–P distances of 2.2993(12) and 2.2721(11) Å, respectively and a corresponding P–Rh–P angle of 78.85(4)°. The central P atom of the P_5 chain (P(3)) also acts as phosphine donor to the formally Rh(III) centre with a Rh–P distance of 2.3189(12) Å. The resulting geometry at Rh is best described as distorted square pyramidal in which one of the phosphides (P(1)) adopts the pseudo-axial position. The dissymetry about the RhN_2P_2 plane is reflected in the Rh–N distances as the N *trans* to phosphide (N(2)) gives rise to a longer Rh–N distance (2.152(3) Å) than the N *trans* to the phosphine donor, N(1) (2.140(3) Å). The P–P bond distances in the P_5 chain fall into two ranges with those adjacent the phosphide donors averaging 2.2234(16) Å and those adjacent the phosphine donor averaging 2.1879(16) Å.

Monitoring the generation of **3** reveals that in addition to the resonances of **3**, signals derived from a second species are also initially observed. This species exhibits a pattern of complex resonances ranging from 45 to −25 ppm, of similar symmetry to those seen for **2**. These resonances diminish in intensity with time as the resonances derived from **3** grow stronger over the course of the reaction. These data support the view that coordination of P_5Et_5 precedes oxidative addition. The differing nature of the products of the reactions of P_5R_5 (R = Ph, Et) is attributable to

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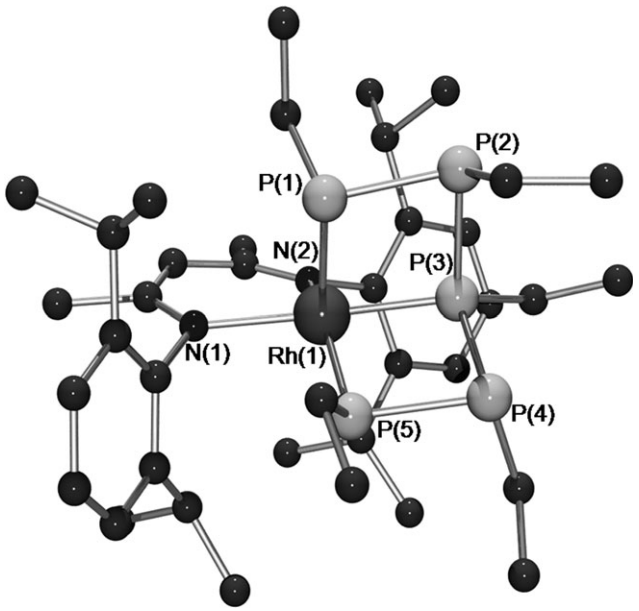

Fig. 3 POV-Ray drawing of **3**, hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Rh–P(1) 2.2993(12) Rh–P(3) 2.2721(11), Rh(1)–P(5) 2.3189(12), Rh–N(2) 2.152(3), Rh–N(1) 2.140(3), P(1)–P(2) 2.2226(16), P(2)–P(3) 2.1890(16), P(3)–P(4) 2.1858(15), P(4)–P(5) 2.2243(15); N(2)–Rh–N(1) 89.93(13), N(1)–Rh–P(3) 168.16(9), N(2)–Rh–P(3) 101.93(9), N(1)–Rh–P(1) 92.26(9), N(2)–Rh–P(1) 115.67(10), P(3)–Rh–P(1) 78.85(4), N(1)–Rh–P(5) 95.22(9), N(2)–Rh–P(5) 152.56(10), P(3)–Rh–P(5) 77.36(4), P(1)–Rh–P(5) 91.31(4), N(1)–Rh–P(3) 168.16(9), P(2)–P(1)–Rh(1) 97.05(5), P(3)–P(2)–P(1) 82.30(6), P(4)–P(3)–P(2) 106.23(6), P(3)–P(4)–P(5) 81.17(5), P(4)–P(5)–Rh(1) 99.39(5).

the relative donor ability and the lesser steric requirements of ethyl substituents *vs.* phenyl groups. Oxidative addition of the electron donating P_5Et_5 stabilizes the Rh(III) product **3** whereas the less electron rich P_5Ph_5 favors reductive elimination and thus a Rh(I) product.

Together, the isolation of complexes **2** and **3** provide rare evidence of the P–P bond activation of an oligophosphine without fragmentation. The potential of such P–P bond activation processes to offer stoichiometric and perhaps catalytic routes to oligophosphine derivatives is currently under investigation.

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Notes and references

§ *Preparation* of **2**: P_5Ph_5 (86 mg, 0.159 mmol) was added to a solution of (**1**) (100 mg, 0.159 mmol) in 5 mL of toluene. The mixture was allowed to stir overnight. Volatiles were removed and 5 mL of cold pentane was added. The solution was filtered and RhNacNac(P_5Ph_5) was isolated as a red powder (120 mg, 0.116 mmol, 73% yield). Anal. Calc. for $RhP_5N_2C_{59}H_{66}$ (%): C: 66.79, H: 6.27, N: 2.64; found: C: 66.65, H: 6.47, N: 2.42. ^{1}H NMR (C_6D_6) δ: 0.49 (3H, d, J = 6.7 Hz), 1.01 (3H, d, J = 6.6 Hz), 1.16 (3H, d, J = 6.8 Hz), 1.35 (3H, d, J = 6.9 Hz), 1.40 (3H, d, J = 6.8 Hz), 1.51 (3H, s), 1.55 (3H, s), 1.78 (3H, d, J = 6.8 Hz), 2.18 (3H, d, J = 6.8 Hz), 2.82 (1H, sept, J = 6.7 Hz), 3.76 (1H, sept, J = 6.8 Hz), 4.46 (1H, sept, J = 6.9 Hz), 4.83 (1H, sept, J = 6.9 Hz), 5.04 (1H, s), 6.20 (1H, d, J = 7.5 Hz), 6.29 (2H, t, J = 7.5 Hz), 6.33 (2H, t, J = 7.2 Hz), 6.41 (1H, t, J = 7.2 Hz), 6.45–6.51 (2H, m), 6.60 (3H, m), 6.74–6.85 (6H, m), 6.90–7.03 (3H, m), 7.11 (1H, d, J = 7.4 Hz), 7.21 (1H, d, J = 7.8 Hz), 7.24 (1H, t, J = 7.4 Hz), 7.36 (2H, t, J = 7.3 Hz), 7.69 (4H, t, J = 8.6 Hz), 9.51 (2H, t, J = 7.5 Hz). ^{31}P NMR (C_6D_6) δ: −16.1 (ddddd, J = 200.5 Hz, J = 213.4 Hz, J = 18.3 Hz, J = 12.0 Hz, J = 5.9 Hz), −1.4 (ddddd, J = 364.0, J = 265.3 Hz, J = 9.4 Hz, J = 18.3 Hz, J = 9.0 Hz), 15.5 (ddddd, J = 265.3 Hz, J = 198.0 Hz, J = 12.0 Hz, J = 8.7 Hz, J = 2.1 Hz), 31.2 (ddddd, J = 200.5 Hz, J = 198.0 Hz, J = 150.0 Hz, J = 9.4 Hz, J = 3.3 Hz), 49.3 (ddddd, J = 364.0 Hz, J = 213.4 Hz, J = 156.6 Hz, J = 8.7 Hz, J = 3.3 Hz).

¶ X-Ray quality crystals of **2** were grown from a concentrated hexane solution at room temperature. $C_{62}H_{73}N_2P_5Rh$; space group: monoclinic, $P2_1/c$, a = 12.652(2), b = 23.285(4), c = 20.121(4), β = 105.382(2)°, V = 5715.3(18), Z = 4. Data/variables 13 164/631; R = 0.0568, R_w = 0.1090, GOF = 1.022; CCDC 669401.

‖ *Preparation* of **3**: P_5Et_5 (28 mg, 0.079 mmol) was added to a solution of **1** (50 mg, 0.079 mmol) in 5 mL of toluene. The mixture was allowed to stir for two weeks. Volatiles were removed *in vacuo* and 0.5 mL of pentane was added to the residue. This solution was stored at −35 °C for three days and the solvent was decanted, leaving a dark red powder (28 mg, 43% yield). Anal. Calc. for $RhP_5N_2C_{39}H_{66}$ (%): C: 57.07, H: 8.11, N: 3.41; found: C: 57.31, H: 8.47, N: 3.18. ^{1}H NMR (C_6D_6) δ: 0.38 (2H, m), 0.52 (3H, dt, J_{P-H} = 16.6 Hz, J = 7.3 Hz), 0.96–1.03 (6H, m), 1.06 (3H, d, J = 6.7 Hz), 1.10 (3H, d, J = 6.7 Hz), 1.11–1.35 (12 H, m), 1.32 (3H, d, J = 6.7 Hz), 1.37 (3H, d, J = 6.7 Hz), 1.39 (3H, d, J = 6.7 Hz), 1.70 (3H, d, J = 6.7 Hz), 1.72 (3H, s), 1.73 (3H, d, J = 6.7 Hz), 1.78 (3H, s), 1.81 (3H, d, J = 6.7 Hz), 2.25 (1H, m), 2.48 (1H, m), 3.12 (1H, sept, J = 6.7 Hz), 3.57 (1H, sept, J = 6.7 Hz), 3.61 (1H, sept, J = 6.7 Hz), 3.65 (1H, sept, J = 6.7 Hz), 4.94 (1H, s), 7.02 (1H, dd, J = 7.3 Hz, J = 1.0 Hz), 7.12 (1H, t, J = 7.8 Hz), 7.15–7.21 (2H, m, obscured by C_6D_6), 7.30 (1H, dd, J = 7.8 Hz, J = 1.6 Hz). ^{31}P NMR (C_6D_6) δ: −110.0 (ddddd, J = 259.2 Hz, J = 210.6 Hz, J = 174.2 Hz, J = 85.1 Hz, J = 36.4 Hz), −15.9 (dd, J = 147.0 Hz, J = 74.9 Hz), 18.5 (dd, J = 212.2 Hz, J = 166.9 Hz), 20.9 (dd, J = 174.4 Hz, J = 147.8 Hz), 79.7 (ddd, J = 168.0 Hz, 60.8 Hz, J = 38.7 Hz).

** X-Ray quality crystals of **3** were grown by slow evaporation from 1 : 1 pentane–Et_2O. $C_{39}H_{66}N_2P_5Rh$; space group: monoclinic, $P2_1/n$, a = 12.7417(15), b = 17.733(2), c = 19.684(2), β = 103.2450(10)°, V = 4329.3(9), Z = 4. data/variables 7614/424; R = 0.0579, R_w = 0.1480, GOF = 1.020; CCDC 669402.

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