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COMMUNICATION

Access to catenated and branched polyphosphorus ligands and coordination complexes *via* a tri(pyrazolyl)phosphane[†][‡]

Kai-Oliver Feldmann,^{ab} Roland Fröhlich^c and Jan J. Weigand^{*a}

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We report a convenient and smooth protocol for the highyielding synthesis of a triphosphane and an *iso*-tetraphosphane from a readily accessible tri(pyrazolyl)phosphane. The products are obtained from a one-pot reaction at room temperature and form complexes with the $Fe(CO)_4$ -fragment.

Chemists have developed synthetic strategies to access essentially any C-C bonded molecular framework. Many analogies have been described between carbon and phosphorus that can be justified by the diagonal relationship between these elements in the periodic table.¹ Although the P–P bond energy (200 kJ mol⁻¹) is relatively low compared to the C-C bond (350 kJ mol⁻¹),² a significant number of polyphosphanes,³ polyphosphide anions⁴ and polyphosphorus cations⁵ has been isolated. Nevertheless, the number of P-P bonded frameworks is small compared to the vast array of C-C bonded compounds.⁶ The preparation of organo-substituted polyphosphanes with more than one P-P bond is challenging except for cyclo-polyphosphanes $(\mathbf{R}_n \mathbf{P}_n)$ (n = 3-6). Synthetic procedures for acyclic and branched polyphosphorus compounds are limited. Some transition metal⁷ and main group element mediated approaches have been described. Scheme 1 shows selected examples. iso-Tetraphosphanes can be prepared from P_1 units by reacting halophosphanes with either phosphides (formation of 1)⁸ or silvlphosphanes (formation of 2)⁹ in a metathesis reaction. Triphosphanes have also been prepared by the reaction of a *cyclo*-tetrapnictane derivative 3 with MeI as an electrophile to yield triphosphane 4.¹⁰ Derivative 5 is obtained via an aminolysis reaction involving a sec. phosphane and an aminophosphane.¹¹ While these examples¹² are viable methods for the preparation of triphosphanes and iso-tetraphosphanes they are either low yielding, require harsh conditions such as elevated temperatures or highly basic media



Scheme 1 Examples of the preparation of tri- and iso-tetraphosphanes.

or rely on preformed triphosphane fragments and use of demanding reagents. These limitations mainly prevented the establishment of polyphosphane chemistry to be used in synthetic and coordination chemistry. This contribution introduces an unprecedented and facile way for the preparation of a triphosphane (6) and an iso-tetraphosphane (1) and demonstrates that the hitherto believed instability of 1 may have been overestimated.8 Our approach is based on the known phosphanylation reaction of primary and secondary phosphanes utilizing alkylaminophosphanes to generate P-P bonds along with the elimination of the corresponding sec. amine. These reactions typically require high reaction temperatures and give the targeted phosphanes often in low to moderate vields only.^{13,11} It has been shown that phosphanylation reactions using alkylaminophosphanes in polymer supported syntheses of DNA are catalyzed by azoles. In these reactions azole substituted phosphorus derivatives were identified as reactive intermediates.¹⁴ During our investigation on the reactivity of highly charged phosphorus cations with nucleophiles, we realized that the P-N bond in pyrazolylphosphane derivatives can be easily cleaved.¹⁵ In this context, we addressed the question if this reactivity pattern can be applied for P-P bond formation, using pyrazolyl-substituted phosphanes as easily accessible P_1 units in combination with secondary phosphanes.

Tris-(3,5-dimethyl-1-pyrazolyl)phosphane (8) was chosen as a P₁ source in the reaction with two eq. of Cy_2PH (Cy = cyclohexyl). We anticipated the generation of two new P–P bonds *via* the elimination of two eq. of 3,5-dimethylpyrazole (7) to yield triphosphane 6 (Scheme 2a). The formation of 6 proceeds remarkably efficient at room temperature and the product can be conveniently isolated by filtration and washing

^a Department of Inorganic and Analytical Chemistry, University of Münster, Corrensstr. 30, 48149 Münster, Germany. E-mail: jweigand@uni-muenster.de; Fax: +49-215-8333126; Tel: +49-215-8336074

^b Graduate School of Chemistry, University of Münster, Correspondence of Münster, Correspondence of Münster,

Corrensstr. 30, 48149 Münster, Germany

^c Department of Organic Chemistry, University of Münster, Corrensstr. 40, 48149 Münster, Germany

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Scheme 2 Preparation of triphosphane 6 and *iso*-tetraphosphane 1 from 8 and Cy_2PH . (a) 2 Cy_2PH , -2 3,5-dimethylpyrazole (7), CH_3CN , RT, 15 h, 91%; (b) 3 Cy_2PH , -3 7, CH_3CN , RT, 7 d, 95%.

with CH₃CN. Compound 6 was obtained as analytically pure colourless material in high yield (91%). In a similar approach iso-tetraphosphane 1 was obtained reacting 8 with three eq. of Cy₂PH (Scheme 2b).¹⁶ This reaction proceeds via the elimination of three eq. of 7 and formation of three P-P bonds. As is in the case of 6 the isolation of 1 only involves filtration and washing with CH₃CN to yield an analytically pure colourless product in excellent yield (95%). Compound 1 was previously obtained from the metathesis reaction of K[P(SiMe₃)₂] with three eq. of Cy₂PCl in very low yield (10%, Scheme 1 top reaction) and was only characterized by ³¹P NMR investigations and a melting point (86 °C). It was stated that 1 perishes slowly in the solid state even under inert conditions and decomposes in hot toluene (70 °C) quickly to Cy₂P-PCy₂ and Cy₂PH via an unknown mechanism.⁸ In contrast, we found that analytically pure 1 appears to be indefinitely stable in the solid state (under Ar or N_2) and has a defined melting range (169–171 °C). Slight melting-associated decomposition was only observed when 1 was heated at elevated temperatures (>175 °C) for a longer period of time. Solutions of 1 in toluene were stable for more than four weeks and heating to 70 °C (60 min) did not show any sign of decomposition.

The ${}^{31}P{}^{1}H{}$ NMR spectrum of **6** reveals an A₂B spin system $(\delta_{\rm A} = 1.9 \text{ ppm}, \delta_{\rm B} = 29.0 \text{ ppm}; {}^{1}J(P_{\rm A}P_{\rm B}) = -271.8 \text{ Hz}, \Delta \delta/J_{\rm AB} \approx 19,300 \text{ K}, C_6 D_6)^{16}$ with eight lines¹⁷ in an approximate intensity ratio of 2 : 1. For compound 1 a characteristic higher order AM₃ spin system ($\delta_A = -108.9$ ppm, $\delta_M =$ $-5.2 \text{ ppm}; {}^{1}J(P_{A}P_{M}) = -361.9 \text{ Hz}, \Delta \delta / J_{AM} \approx 49,300 \text{ K}, C_{6}D_{6})^{16}$ is observed consistent with previously reported data.8 The pronounced up-field shift of the resonance of the central phosphorus atom in 6 in comparison to the respective nucleus in 1 can be explained by the electron withdrawing effect of the pyrazole substituent. Except for a very few examples,^{18,10} the coordination chemistry of tri- and tetraphosphanes as ligands is not developed mainly due to the belief that these ligands are too unstable^{18b} and require labour intensive and specialized synthetic procedures. In contrast, we have now found that polyphosphanes 6 and 1 react readily with $Fe_2(CO)_9$ to form the corresponding iron-complexes 9 and 10 with an intact ligand framework. The reaction is accompanied by the formation of $Fe(CO)_5$ (Scheme 3). The reactions proceed rather cleanly (>80% of the desired product in solution by NMR), however the isolated yields of the complexes 9 (56%) and 10 (39%) are moderate.¹⁶ Nevertheless, the formation and stability of complexes 9 and 10 is remarkable, as it was reported that transition metal polyphosphane complexes could not be prepared via coordination of the free polyphosphane, but have to be assembled at a transition metal.^{18b} Wright and co-workers were the first to prove that a triphosphane can indeed be



Scheme 3 Preparation of complexes 9 and 10 from 6 and 1, respectively. (a) $Fe_2(CO)_9$, $-Fe(CO)_5$, THF, RT, 12 h, 56%; (b) $Fe_2(CO)_9$, $-Fe(CO)_5$, THF, RT, 12 h, 39%.

coordinated intact to a transition metal.¹⁰ The isolation of complex 10 shows that this is also valid for *iso*-tetraphosphanes. The complexes 9 and 10 are characterized by distinct carbonyl stretching vibrations (9: 2044, 1972, 1930, 1916(sh); 10: 2039, 1969, 1920(sh) cm⁻¹), which are reminiscent of the two a_1 and one *e* stretching vibrations of C_{3v} symmetric [Fe(CO)]₄¹⁹ moieties but indicative of the overall lower symmetry of the compounds.¹⁶ The ¹³C{¹H} NMR spectrum displays characteristic multiplets for the carbonyl ligands in 9 ($\delta = 213.8$ ppm) and 10 ($\delta = 215.8$ ppm), respectively.²⁰ The experimental and fitted ${}^{31}P{}^{1}H$ NMR spectra along with the spin system and chemical shifts are shown in Fig. 1. The low-field shift of the coordinated P atom (9: $\delta = 85.0$ ppm; 10: $\delta = 97.0$ ppm) in comparison to the respective polyphosphane is a characteristic feature of this type of complexes and was previously observed for related compounds.^{18b} Both compounds were also crystallographically characterized. The molecular structures of complexes 9 and 10 along with selected bond lengths and angles are given in Fig. 2. Compound 10 represents the first structurally



Fig. 1 ³¹P{¹H} NMR spectra (C₆D₆, 300 K) of the complexes **9** and **10**. (a) AMX spin system for **9**: $\delta_A = -1.4$, $\delta_M = 33.3$, $\delta_x = 85.0$; ¹*J*(P_AP_M) = -381.8 Hz, ¹*J*(P_MP_X) = -325.6 Hz, ²*J*(P_AP_X) = 16.5 Hz; (b) AM₂X spin system for **10**: $\delta_A = -70.7$, $\delta_M = 15.4$, $\delta_x = 97.0$; ¹*J*(P_AP_M) = -464.9 Hz, ¹*J*(P_AP_X) = -345.0 Hz, ²*J*(P_MP_X) = 45.8 Hz. Expansions (inset) show the experimental (up) and fitted spectra (down).



Fig. 2 ORTEP plot of the molecular structures of compounds (a) **9** and (b) **10**. Thermal ellipsoids are drawn at 50% probability (hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: **9**: P1–Fe 2.2765(7), P1–P2 2.2384(9), P2–P3 2.2133(9), P2–N31 1.736(2), N31–N32 1.381(3), P2–P1–Fe 105.65(3), N31–P2–P3 109.55(8); N31–P2–P1 100.51(8), P3–P2–P1 106.72(4); **10**: P1–Fe 2.284(1), P1–P2 2.221(1), P2–P4 2.193(1), P2–P3 2.210(1), N31–N32 1.381(3), P2–P1–Fe 108.76(4), P4–P2–P3 127.34(5); P4–P2–P1 104.08(5), P3–P2–P1 106.88(5).

characterized example of a metal complex of an *iso*-tetraphosphane. In both complexes, the Fe(CO)₄ moiety coordinates to a terminal phosphorus atom. This mode of coordination was reported to be thermodynamically favourable over the coordination of the central phosphorus atom for the related triphosphane complex $[Ph_2PP(Ph)P(Ph)_2Fe(CO)_4]$.^{18b} Notably, the polyphosphorus ligands occupy the axial position of the pseudo trigonal bipyramidal coordination sphere of the iron atom. Apparently the coordination site is determined by electronic rather than steric factors which may be indicative of the low π -acceptor properties of the polyphosphane ligands.^{21,18c}

In summary, a highly efficient method affords symmetric tri- and *iso*-tetraphosphanes in very high yields. This simple protocol should allow for the systematic development of a plethora of other tri- and *iso*-tetraphosphanes with a highly diverse substitution pattern. We are currently investigating this type of P–P bond formation using pyrazolyl-substituted phosphanes as easily accessible P₁ units in combination with a series of primary and secondary phosphanes to access hitherto unknown structural motives in polyphosphane chemistry. In addition, this simple approach allows a systematic investigation of the coordination chemistry of polyphosphane ligands. We are especially interested in using triphosphanes and *iso*-tetraphosphanes as polydentate, chelating ligands and explore their properties in the field of homogenous catalysis.

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