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Synthesis and characterization of 1-(3,5-di-*tert*-butyl)pyrazolyldiphenylphosphine and its gold(I) complex

Aibing Xia [a,*], Corey Seward [b], Mariza Voges [a]

[a] *Department of Chemistry, Mount Saint Vincent University, Halifax, Nova Scotia, Canada B3M 2J6*
[b] *Department of Chemistry, Saint Mary's University, Halifax, Nova Scotia, Canada B3H 3C3*

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Abstract

1-(3,5-Di-*tert*-butyl)pyrazolyldiphenylphosphine was prepared from 3,5-di-*tert*-butyl)pyrazole and chlorodiphenylphosphine. It reacted with $(Me_2S)AuCl$ to afford a Au(I) complex bearing the pyrazolylphosphine ligand in a monodentate coordination mode.

Keywords: Unsymmetrical ligands; Hemilabile property; Pyrazolylphosphine; Gold(I) complex

Unsymmetrical P,N ligands, which contain one phosphorus donor and one nitrogen donor, have attracted increasing attention recently due to their bonding versatility, unique reactivity, and catalytic applications as hemilabile ligands [1,2]. Pyrazolylphosphines (Fig. 1), with a P–N bond between one pyrazolyl group and one phosphino group, were prepared by Peterson and co-workers over 30 years ago [3]. They are air- and moisture-sensitive, and react readily with protic species such as alcohols through the nitrogen atom at the 2-position (N(2)) of the pyrazolyl group, leading to cleavage of the P–N bond. Therefore even though they were easy to prepare and isolate, their applications as ancillary ligands were scarce and mainly limited to mid-transition metal carbonyl complexes, in which the pyrazolylphosphine ligands acted as either monodentate or bidentate donors [4]. In these complexes, the electron-withdrawing carbonyls make the N(2) atom in the pyrazolyl group less nucleophilic, which stabilizes the pyrazolylphosphine ligands. But stable late transition-metal complexes bearing pyrazolylphosphine ligands are even more elusive. Recently Ros and co-workers reacted[$RuCl_2$(*p*-cymene)]$_2$ with 1-(3,5-di-methyl)pyrazolyldiphenylphosphine, $PPh_2(3,5\text{-}Me_2pz)$ [5]. However, the targeted product $RuCl_2$(*p*-cymene)($PPh_2(3,5\text{-}Me_2pz)$) was always contaminated by by-products such as [RuCl(*p*-cymene)($3,5\text{-}Me_2pzH$)(PPh_2OH)]Cl, indicating hydrolysis of the pyrazolylphosphine ligand via P–N bond cleavage. As electron-rich late transition metal complexes are widely used in a variety of important catalytic processes [6], it is desirable to employ electron-rich pyrazolylphosphines as ancillary ligands in late transition-metals. Here we report the synthesis, characterization, and application of a novel pyrazolylphosphine compound, 1-(3,5-di-*tert*-butyl)pyrazolyldiphenylphosphine, which contains bulky *tert*-butyl substituents in the pyrazolyl moiety and shows improved stability over its smaller analogues.

Reaction of chlorodiphenylphosphine with 3,5-di-*tert*-butylpyrazole [7] in diethyl ether in the presence of 4-*N*,*N*-dimethylaminopyridine (DMAP) afforded 1-(3,5-di-*tert*-butyl)pyrazolyldiphenylphosphine, $PPh_2(3,5\text{-}{}^tBu_2pz)$, in quantitative yield (Eq. (1)). The resultant compound can be easily obtained after filtering of the pyridinium salt and removal of solvent under reduced pressure [8]. $PPh_2(3,5\text{-}{}^tBu_2pz)$ demonstrated drastically improved stability over its smaller analogues. While $PPh_2(3,5\text{-}Me_2pz)$ and PPh_2pz are very air- and moisture-sensitive, $PPh_2({}^tBu_2pz)$ may be recrystallized from bench diethyl ether in air [9].

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[*] Corresponding author. Tel.: +1 902 457 6543.
E-mail address: aibing.xia@msvu.ca (A. Xia).

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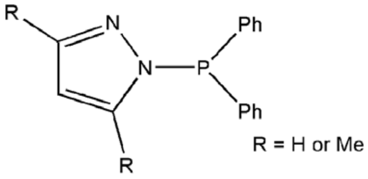
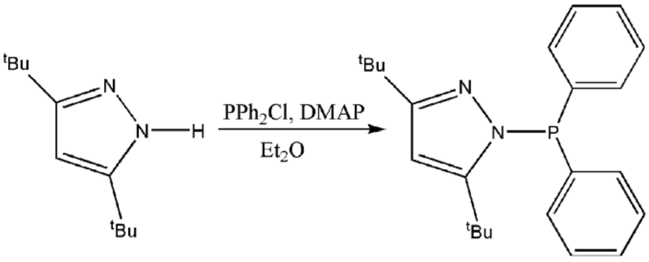


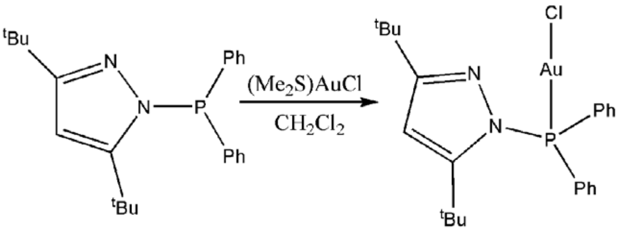
Fig. 1. Pyrazolylphosphines.

In addition, $PPh_2(3,5\text{-}^tBu_2pz)$ showed good thermal stability and could be sublimed under vacuum. In a GC/MS analysis of the compound, one single peak was observed with a molecular mass of 364. As $PPh_2(3,5\text{-}^tBu_2pz)$ is more electron-rich than $PPh_2(3,5\text{-}Me_2pz)$, the improved stability of the more bulky compound can be attributed to the steric factor instead of an electronic one.



(1)

Addition of $PPh_2(3,5\text{-}^tBu_2pz)$ to a suspension of $(Me_2S)AuCl$ (prepared from reaction of Me_2S and $HAuCl_4$ in MeOH) in CH_2Cl_2 led to a clear colorless solution at room temperature (Eq. (2)). The solution showed a single peak at 75.38 ppm in ^{31}P NMR spectrum, indicating a single phosphorus-containing product. The 29.10 ppm downfield shift after coordination of the ligand to Au(I) is similar to that of its methyl analogues [4–6]. The ^1H NMR spectrum of the Au(I) complex showed that chemical shifts of the methine (CH) and two *tert*-butyl groups in the pyrazolyl moiety are slightly changed upon coordination [8,10]. The methine hydrogen showed a doublet with a coupling constant of 2.75 Hz, reflecting the long-range interaction between phosphorus and hydrogen nuclei [3,4].



(2)

Recrystallization of the Au(I) complex in CH_2Cl_2/hexanes at −30 °C afforded single crystals suitable for X-ray analysis (Fig. 2) [11]. In solid state, the Au(I) complex is monomeric with an almost perfectly linear geometry around Au(I) (P–Au–Cl angle = 176.93(5)°). The Au–P–N(1) angle of 109.43(16)° is ideal for the tetrahedral phosphorus atom. The Au–P length of 2.228(1) Å and Au–Cl bond length of 2.276(1) Å are virtually identical to those of $(PPh_3)AuCl$ [12]. In the new pyrazolylphoshine, the N(2) atom on the pyrazolyl group is flanked by two phenyl groups and an adjacent bulky *tert*-butyl group, which gives rise to improved stability against hydrolysis and oxidation.

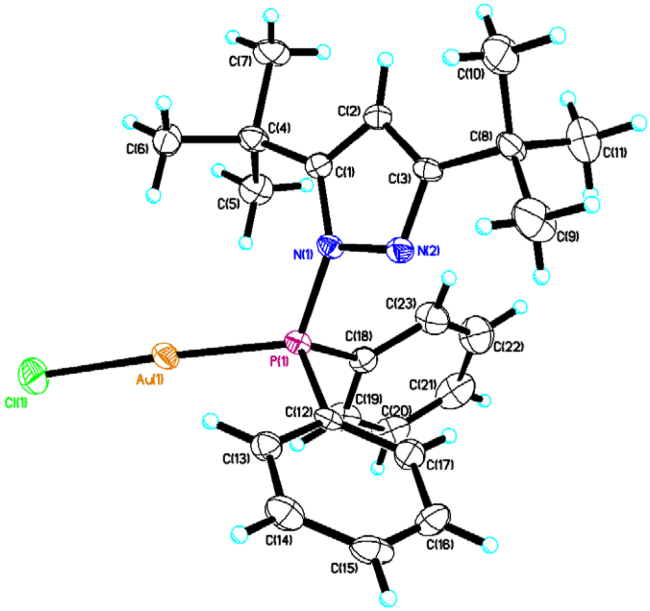


Fig. 2. Molecular Structure of $(PPh_2(3,5\text{-}^tBu_2pz))AuCl$ (thermal ellipsoids drawn at the 30% probability). Selected bond lengths (Å) and angles (°): Au(1)–P(1) 2.228(1), Au(1)–Cl(1) 2.276(1), P(1)–N(1) 1.725(4), P(1)–C(18) 1.803(5), P(1)–C(12) 1.807(5); P(1)–Au(1)–Cl(1) 176.93(5), N(1)–P(1)–Au(1) 116.61(14), C(18)–P(1)–Au(1) 114.96(15), C(12)–P(1)–Au(1) 109.43(16), N(1)–P(1)–C(18) 103.7(2), N(1)–P(1)–C(12) 104.97(18), C(18)–P(1)–C(12) 106.3(2).

In summary, we demonstrated that through steric control, it is feasible to prepare electron-rich and stable pyrazolylphosphine compounds. The desirable steric and electronic features, combined with the ease of preparation and isolation of the pyrazolylphosphines, may facilitate their broader use as ancillary ligands in late transition metal complexes. The Au(I) complex reported here is the first fully characterized pyrazolyphosphine-based late transition metal complex that does not contain electron-withdrawing carbonyl ligands. The catalytic applications of the novel pyrazolylphosphine and related compounds are under way.

Acknowledgement

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Appendix A. Supplementary material

CCDC 652244 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2007.08.012.

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[8] Characterization of PPh$_2$(3,5-^{t}Bu$_2$pz): M.p. 136–138 °C. Anal. Calc. for $C_{23}H_{29}N_2P$: C, 75.80; H, 8.02; N, 7.69. Found: C, 75.68; H, 8.29; N, 7.66%. ^{1}H (CDCl$_3$, 250.14 MHz): δ 1.20 (s, 9H, CH$_3$), 1.52 (s, 9H, CH$_3$), 5.88 (d, $^4J_{P,H} = 2.75$ Hz, CH), 7.29–7.47 (m, 10H, C$_6$H$_5$), ^{31}P{^{1}H} (CDCl$_3$, 101.26 MHz): δ 46.28. IR (KBr, cm^{-1}): 3060 w, 2962 s, 1540 s, 1479 m, 1434 m, 1361 s, 1249 s, 1201 m, 1128 s, 1110 m, 988 m, 744 s, 696 s, 511 m.

[9] No hydrolysis products (3,5-^{t}Bu$_2$pzH and PPh$_2$OH) were detected, but about 5% oxidation product (phosphine oxide) was observed in a GC/MS analysis.

[10] Characterization of (PPh$_2$(3,5-^{t}Bu$_2$pz))AuCl: M.p. 194–196 °C. Anal. Calc. for $C_{23}H_{29}AuClN_2P$: C, 46.28; H, 4.90; N, 4.69. Found: C, 46.64; H, 4.76; N, 4.50%. ^{1}H (CDCl$_3$, 250.14 MHz): δ 1.13 (s, 9H, CH$_3$), 1.68 (s, 9H, CH$_3$), 6.10 (d, $^4J_{P,H} = 2.35$ Hz, CH), 7.42–7.60 (m, 10H, C$_6$H$_5$), ^{31}P{^{1}H} (CDCl$_3$, 101.26 MHz): δ 75.38. IR(KBr, cm^{-1}): 3057 w, 2966 s, 1549 s, 1437 s, 1253 s, 1190 s, 1103, 984 m, 750 m, 743 s, 692 s, 519 s.

[11] The crystal data for (PPh$_2$(3,5-^{t}Bu$_2$pz))AuCl were collected on a Siemens SMART diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Crystal data: $C_{23}H_{29}AuClN_2P$, $M = 596.87$, monoclinic, $C2/c$, $Z = 8$, $T = 243$ K, $a = 21.770(4)$ Å, $b = 16.623(3)$ Å, $c = 16.112(3)$ Å, $\alpha = \gamma = 90°$, $\beta = 124.698(2)°$. $V = 4793.5\ (14)$ Å^3, $D_{calc} = 1.654$ Mg/m^3, $\mu = 6.327$ mm^{-1}, $F(000) = 2336$. Refinement method was full-matrix least squares on F^2 using SHELXTL-97 program, 11825 observed reflections, 3445 independent reflections ($R_{int} = 0.0816$) with $R_1 = 0.0324$, $wR_2 = 0.0579$.

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