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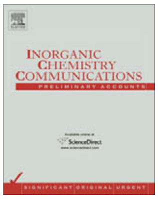

Bis(3,5-dimethylpyrazol-1-yl)alkanones and their reactivity with $[PdCl_2(NCMe)_2]$: Isolation of bis(3,5-dimethylpyrazol-1-yl)propan-1-one palladium(II) chloride and C–H activation of propanone linker

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ABSTRACT

Four new bis(3,5-dimethylpyrazol-1-yl)alkanones were prepared by the reaction of the respective alkanoyl chloride with 3,5-dimethylpyrazole: **L1** from chloropropionyl chloride, **L2** from 4-chlorobutyryl chloride, **L3** from oxalyl chloride and **L4** from adipoyl dichloride; all in moderate yields. Of the four compounds only **L1** successfully reacts with $[PdCl_2(NCMe)_2]$ to yield [PdCl$_2$(**L1**)] in 41% yield, which on heating in toluene leads to C–H activation to produce [PdCl(**L1′**)], where **L1′** is deprotonated **L1**, in very low yield.

Properties of pyrazoles can be modified through functionalization of the NH proton to form a variety of pyrazolyl compounds that could be used as ligands. The most popular of these pyrazolyl ligands are "scorpionates" – pyrazolylborates first developed by Trofimenko [1]. The use of borate linkers gave rise to other linkers, most notably alkyl and aryl linkers [2]. To date various modifications have been made to linkers that have led to different chemical and structural behavior of metal complexes they form. Pons and others have demonstrated that bis(pyrazolyl)alkylamine [3], ether [4] and thioether analogues [5] can function as either bidentate ligands that use the two nitrogen atoms of the ligands or as tridentate ligands that involve the heteroatom in the linker. Such linker binding atoms have allowed the design of tridentate chromium and nickel complexes that catalyze the polymerization or oligomerization of ethylene [6]. Recently we have used carbonylbenzene [7], carbonylpyridine [8], methylbenzene [9] and methylpyridine [10] linkers to prepare mainly bis(pyrazolyl)palladium complexes some of which catalyze oligomerization or polymerization of ethylene. For palladium complexes with pyridine-containing linkers the pyridine nitrogen binds in preference to one of the pyrazolyl units, thus leaving this pyrazolyl unit dangling; however bis(pyrazolylmethyl)pyridine ligands act a tridentate ligand when reacted with nickel(II) halides [11]. We have modified the linkers in our ligands to feature alkylcarbonyl units and herein we report how these new ligands react with $[PdCl_2(NCMe)_2]$.

Reaction of alkyl acyl chlorides with two equivalents of 3, 5-dimethylpyrazole produced 1,3-bis(3,5-dimethylpyrazol-1-ly)-alkylnones (**L1** and **L2**) (Scheme 1) [12]. When the linker is a diacyl chloride even more facile reactions occurred to form bis(pyrazolyl)alkyldiones (**L3** and **L4**) (Scheme 2). Characterization of **L2**–**L4** is provided as Supplementary material.

The ^{1}H NMR spectra of **L1** and **L2** are characterized by two distinct peaks for the protons on the pyrazolyl rings between 5.50 ppm and 6.00 ppm, while the spectra of **L3** and **L4** show only one such peak, in addition to the methyl protons on the pyrazolyl rings and the linker protons. The presence of one or two pyrazolyl peaks is indicative of the symmetrical or otherwise of these compounds. The CH_2 proton peaks differ in chemical shifts for each compound, depending on the number of CH_2 groups on the alkyl carbonyl linker; with the CH_2 protons closest to the carbonyl group appearing more downfield due to the electron-withdrawing effect of the carbonyl group. The presence of carbonyl groups in these compounds was identified by their characteristic stretching frequencies between 1729 and 1712 cm^{-1} in their IR spectra. Single crystal X-ray diffraction confirmed the structures of **L1** and **L4**.

Crystallographic data showed that **L1** and **L4** have two pyrazolyl rings with a linker consisting of two CH_2 groups and a carbonyl group next to one of the pyrazolyl rings (**L1**) (Fig. 1) or two pyrazolyl rings with a linker that consists of two CH_2 groups and a carbonyl next to each pyrazolyl ring (**L4**) (Fig. 2). The two pyrazolyl rings in **L1** are close to being perpendicular to each other with a dihedral angle of 74.23(5)° between the pz planes, whereas the two pyrazolyl rings in **L4** are much closer to being coplanar with

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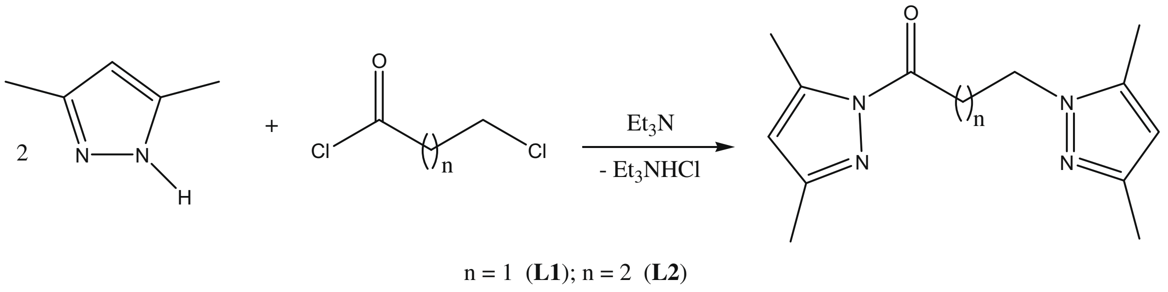
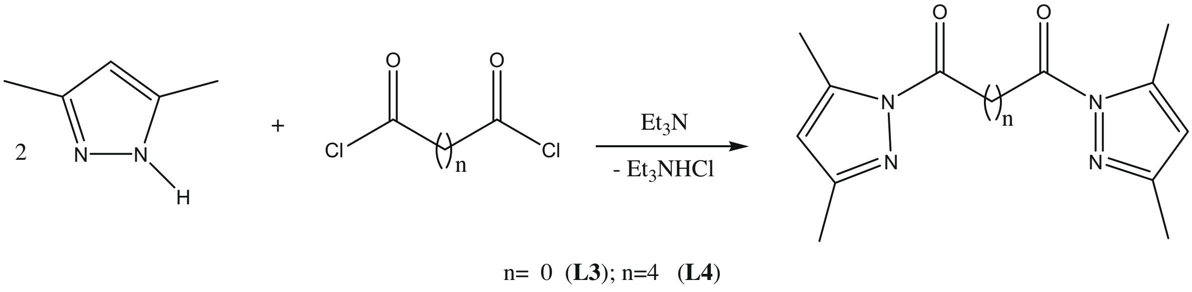


Scheme 1.



Scheme 2.

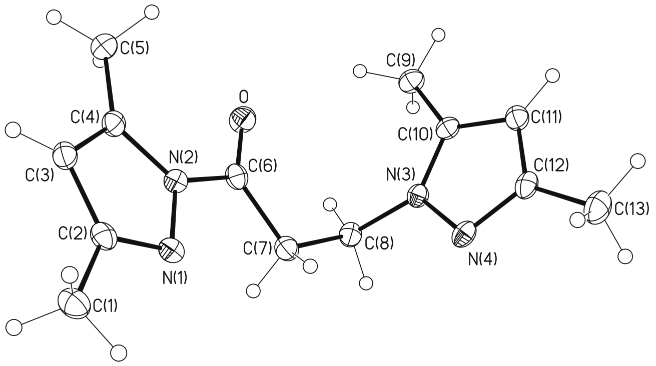


Fig. 1. ORTEP diagram of **L1** with 50% thermal probability ellipsoids.

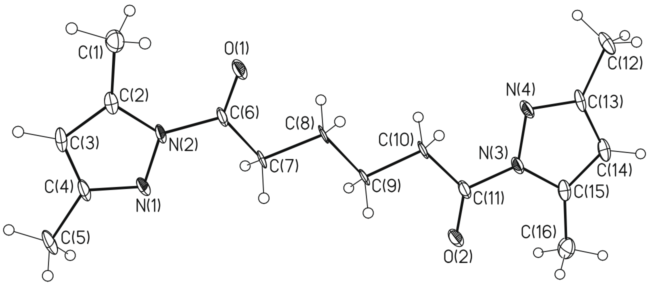


Fig. 2. ORTEP diagram of **L4** with 50% thermal probability ellipsoids.

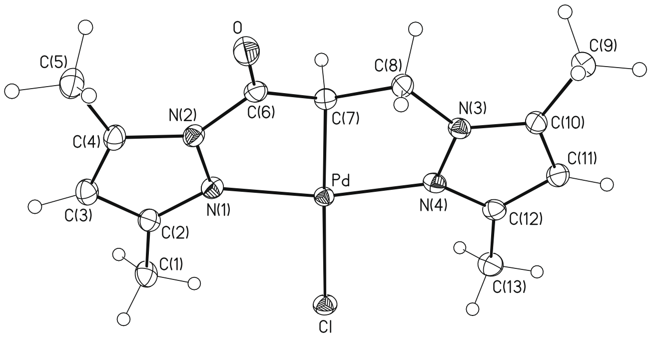
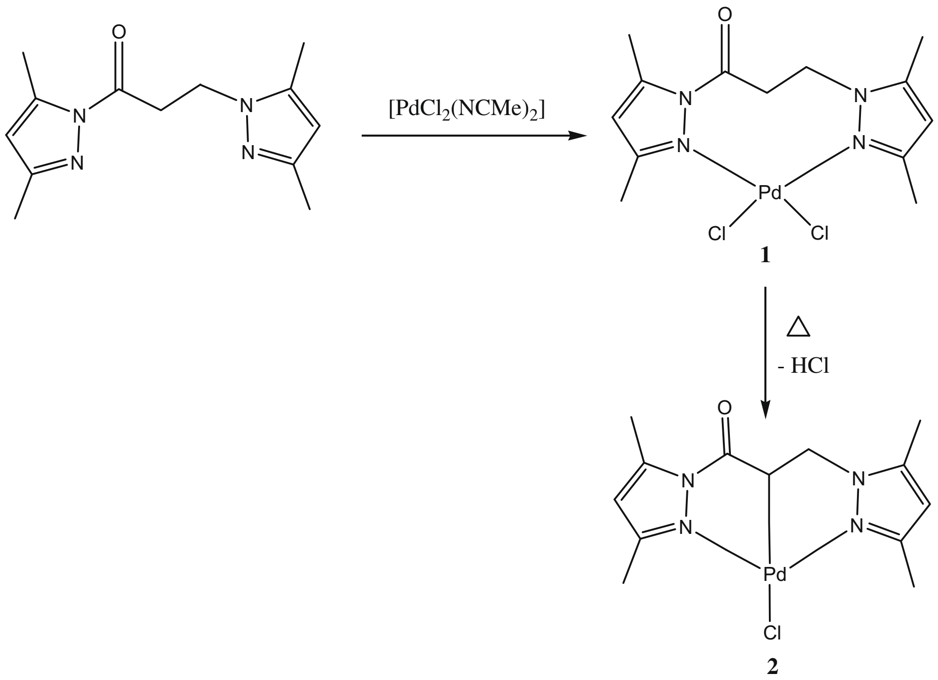


Fig. 3. ORTEP diagram of **2** with 50% thermal probability ellipsoids.

a dihedral angle of 16.28(8)° between them. The N–C(=O) bond length in **L1** is shorter (1.4020(14) Å) than the N–C(=O) bond length of the nitrogen bound to the methylene group (N(3)–C(8) (1.4601 Å) due to conjugation. Other distances agree within experimental error and fall in the usual ranges.

Reaction of **L2**–**L4** with $[PdCl_2(NCMe)_2]$ rapidly led to the formation of $[PdCl_2(3,5\text{-}Me_2pzH)_2]$. We recently reported that the partial hydrolysis of (pyrazol-1-ylcarbonyl)benzene to pyrazole in a palladium complex [13] suggested that the carbonyl linker promotes such hydrolysis. In contrast **L1** produces $[PdCl_2$**L1**$]$ (**1**) but in low yield (41%) and is accompanied by the formation of $[PdCl_2(3,5\text{-}Me_2pzH)_2]$ which indicates that there is partial hydrolysis [14]. The ^{1}H NMR spectrum of complex **1** shows a spectrum pattern similar to that of **L1**, but differs in chemical shifts. There are four methyl protons that have shifted downfield compared to **L1**, and three less intense methyl peaks. One of the latter methyl peaks is more intense than the others, suggesting that a fourth weak methyl peak overlaps with this peak. The two sets of methyl protons imply that there exist two conformers of **1**, boat and chair conformers that are in equilibrium in solution. Two sets of doublets of doublets were observed in the CH_2 region at 4.23 ppm and 5.27 ppm; each attributable to CH_2 protons in the ligand backbone. The NMR data therefore suggest that while the two conformers interconvert through the flipping of the ligand alkyl backbone, the room temperature ^{1}H NMR spectrum is only an average of the four CH_2 groups of the conformers. Pons and co-workers have shown over the years that alkyl linker pyrazolyl complexes readily interchange forms in solution, so this observation is not uncommon [4a,15].

Upon heating **1** transforms into a tridentate [Pd(N^C^N)Cl] complex (**2**), via a C–H activation of the CH_2 next to the carbonyl



Scheme 3.

group thereby eliminating HCl (Scheme 3); albeit it in very low yield and accompanied by decomposition to intractable products. ^{1}H NMR spectrum of **2** clearly shows three doublets of doublets signals between 3.60 ppm and 4.46 ppm that confirm that there are in fact three inequivalent protons in the linker, two from the CH_2 and one from the CH a proton left after the C–H activation and elimination of HCl. The structure of **2** was confirmed by single crystal X-ray crystallography as tridentately bound palladium complex in which a deprotonated **L1** binds the palladium through two N and a C in a distorted square planar geometry (Fig. 3). In this structure the ligand acts a tridentate chelate, coordinating to the metal in a "butterfly" fashion by forming two five-membered metallocycle rings. Ring Pd1–N1–N2–C6–C7 possesses a "twisted" conformation in which atoms C7 and Pd reside above and below the plane of the other three atoms. Ring Pd–N4–N3–C8–C7 is best described as an envelope with C7 as the flap atom. The Pd(II) atom is displaced from the coordination plane defined by atoms Cl, N1, C7, and N4 by 0.0457(7) Å, therefore these five atoms are essentially coplanar. The bond angles around Pd in **2** are: C(7)–Pd–N(4) = 81.54(7)°, C(7)–Pd–N(1) = 81.71(7)°, N(4)–Pd–Cl = 97.22(5)° and N(1)–Pd–Cl = 99.57(5)°. The average Pd–N bond length of 2.040 Å is similar to the average Pd–N bond length of 2.034 Å in the previously reported (3,5-dimethylpyrazolylcarbonyl)pyridine palladium complex [10]. The Pd–Cl bond of 2.4194(5) Å in **2** is slightly longer than average Pd–Cl bond length of 2.33(5) Å obtained from averaging 2055 Pd–Cl bonds in 1268 relevant complexes reported to the CSD [16].

In summary new bis(pyrazolyl)alkanone compounds form from the appropriate acyl chloride linkers and 3,5-dimethylpyrazoles, but compounds with diketone linkers are readily hydrolysed when reacted with $[PdCl_2(NCMe)_2]$. The mono-ketone linker compound, **L1**, however form a dichloride complex which on heating undergoes C–H activation. The metal induced C–H activation in **L1** is therefore a clear indication that **L1** could be used as a tridentate N^C^N ligand to prepare early transition metal ethylene oligomerization or polymerization catalysts and we are currently investigating this.

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Appendix A. Supplementary material

CCDC 740261, 740262 and 740263 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2009.10.036.

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[12] **L1** was prepared from a solution of 3,5-dimethylpyrazole (1.00 g, 10.42 mmol) and 3-chloropropionyl chloride (0.49 mL, 5.21 mmol) in toluene (40 mL), Et_3N (3 mL) was added and this mixture was heated at 80 °C for 24 h. A white precipitate formed which was removed by filtration and evaporated to give an oily residue. The oil was then dissolved in dichloromethane (10 mL), layered with hexane (5 mL) and cooled at −4 °C to give a white solid that was isolated by filtration. Yield = 0.75 g (60%). ^{1}H NMR ($CDCl_3$): δ 2.18 (s, 3H, 3-CH_3, pz); 2.20 (s, 3H, 3-CH_3, pz); 2.27 (s, 3H, 5-CH_3, pz); 2.51 (s, 3H, 5-CH_3, pz); 3.61 (t, $^{3}J_{H-H'}$ = 14.4 Hz, 2H, CH_2-pz); 4.36 (t, $^{3}J_{H-H}$ = 14.4 Hz, 2H, CH_2-CO); 5.75 (s, 1H, CH, pz); 5.94 (s, 1H, CH, pz). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 11.0 (CH_3, pz); 13.5 (CH_3, pz); 13.8 (CH_3, pz), 14.4 (CH_3, pz); 36.2 (CH_2-pz); 43.5 (CH_2-CO); 104.9 (CH, pz); 111.2 (CH, pz); 139.0 (C-CH_3, pz); 143.9 (C-CH_3, pz); 147.6 (C-CH_3, pz); 152.2 (C-CH_3, pz); 171.3 (CO). IR (nujol): $\nu(C{=}O) = 1729\ cm^{-1}$, $(C{=}N) = 1582\ cm^{-1}$. ESI-HRMS: $C_{13}H_{18}N_4O$ Calcd. $[M]^{+} = 247.1559$. Found $[M]^{+} = 247.1559$.

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[14] Complex **1** was prepared from the reaction of **L1** (0.10 g, 3.86 mmol) in toluene (15 mL) in and $[PdCl_2(NCMe)_2]$ (0.10 g, 3.86 mmol) in toluene (15 mL) and stirred for 24 h. An orange-brown precipitate was removed by filtration the orange filtrate obtained evaporated to dryness to give a light brown powder. Yield = 0.05 g (41%). ^{1}H NMR ($CDCl_3$): δ 2.19 (s, 3H, 3-CH_3, pz); 2.35 (s, 3H, 3-CH_3, pz); 2.56 (s, 3H, 5-CH_3, pz); 2.81 (s, 3H, 5-CH_3, pz); 4.23 (t, 2H, CH_2-pz); 5.27 (t, 2H, CH_2-CO); 5.87 (s, 1H, CH, pz); 5.96 (s, 1H, CH, pz). Anal. Calcd. for $C_{13}H_{18}N_4OCl_2Pd$: C, 36.86; H, 4.28; N, 13.23. Found: C, 36.69; H, 4.49; N, 13.08.

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