

Tandem pinacol coupling–rearrangement of aromatic aldehydes with hydrogen catalyzed by a combination of a platinum complex and a polyoxometalate†

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Received (in Cambridge, UK) 3rd July 2007, Accepted 3rd August 2007

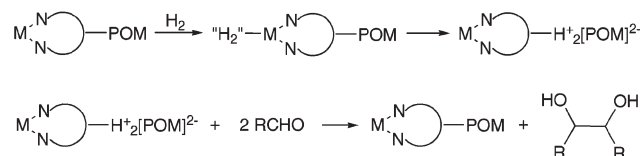
First published as an Advance Article on the web 20th August 2007

DOI: 10.1039/b710100g

Together with a strongly oxidizing polyoxometalate, $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$, $\text{Pt}^{\text{II}}(N-(2,6\text{-diisopropylphenyl})\text{pyrazin-2-ylmethanimine})\text{Cl}_2$ forms a combined catalyst that was active in the tandem pinacol coupling–rearrangement of aryl aldehydes to give mostly the corresponding diarylacetaldehyde in high yields using molecular hydrogen as the reducing agent.

Reductive coupling of carbonyl compounds to diols, introduced by Fittig in 1859 is a classic organic reaction.¹ Now known as the pinacol coupling reaction, it is still a useful synthetic method for carbon–carbon bond coupling. Pinacol coupling has been described for a variety of low-valent metals such as Ti,² V,^{2i,3} Al,⁴ Mg,⁵ Sm,^{2i,6} Cr,^{2i,7} Mn,^{7c,8} and Nb.^{3h,i} The reaction is thought to proceed through a one-electron reduction of a carbonyl group by a pre-reduced metal or metal complex yielding an anion radical.⁹ The anion radical can either dimerize *via* radical–radical coupling or be reduced to a dianion, which then nucleophilically attacks a second carbonyl group. Using low-valent titanium, McMurry, Mukaiyama and Tyrlik found independently that reductive dimerization of aldehydes or ketones can proceed further to give alkenes by a pinacol deoxygenation process.^{2c} A key aspect of these coupling reactions with both metallorganic catalysts and stoichiometric high valent metals is that a significant excess of high potential reducing agents, typically Mg or Zn, are required. This makes these reactions waste intensive and a catalytic method involving hydrogen as terminal reductant would be desirable.

Previous research has revealed that interesting synergies can be obtained in catalyst assemblies comprised of metallorganic compounds and polyoxometalates.¹⁰ Also it has been shown that polyoxometalates, preferably in the presence of noble metals or noble metal complexes, may be reduced with H_2 with formation of electrons and protons.¹¹ The concept at the basis of this paper, summarized in Scheme 1, is that a palladium or platinum complex would activate molecular hydrogen, which in turn would lead to the reduction of a polyoxometalate attached to the transition metal complex by two electrons. Then the catalytically reduced polyoxometalate could enable an electron reduction reaction with

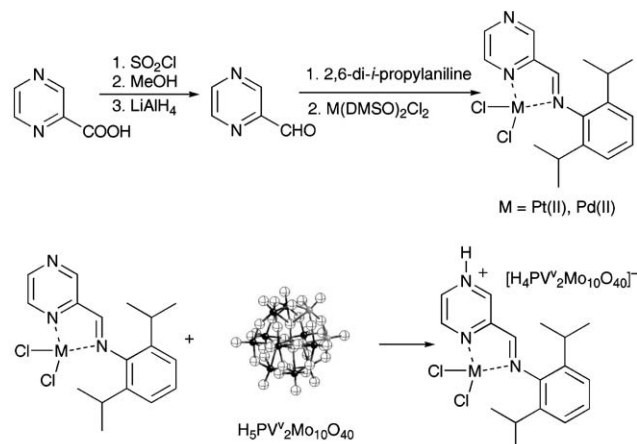


Scheme 1 Generalized picture of pinacol coupling with H_2 using a metal complex–polyoxometalate catalyst.

a carbonyl substrate and would be able to initiate a reductive pinacol coupling reaction.

Based on these principles, we set out to prepare palladium and platinum Schiff base complexes with a distal “handle” to potentially attach an acidic and strongly oxidizing polyoxometalate, $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$, *via* an acid–base interaction according to Scheme 2. Sterically hindered complexes were prepared using isopropyl substituents with a pyridine–imine motif to retain relatively labile coordination sites, that is, to prevent the formation of Pt or Pd complexes coordinated by two bidentate ligands. $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ was chosen because it is a strong oxidant and most likely capable of oxidizing hydrogen.

As detailed in the ESI,† 2,6-diisopropylaniline was condensed with 2-pyrazinecarboxaldehyde to form the bidentate Schiff base ligand that was metalated with $\text{Pt}^{\text{II}}(\text{DMSO})_2\text{Cl}_2$ or $\text{Pd}^{\text{II}}(\text{DMSO})_2\text{Cl}_2$. The X-ray structure of $\text{Pt}^{\text{II}}(N-(2,6\text{-diisopropylphenyl})\text{pyrazin-2-ylmethanimine})\text{Cl}_2$, Pt-1, Fig. 1, revealed the complex to contain a platinum center in a typical square planar



Scheme 2 Preparation of the $\text{M}^{\text{II}}(N-(2,6\text{-diisopropylphenyl})\text{pyrazin-2-ylmethanimine})\text{Cl}_2\text{-H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ binary catalyst.

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† Electronic supplementary information (ESI) available: Details of the experimental methods and catalyst characterization. See DOI: 10.1039/b710100g

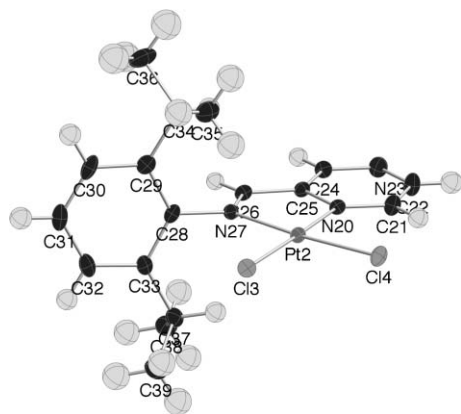


Fig. 1 Ortep drawing of Pt-1.[‡]

coordination mode bound to two chloride anions and one Schiff base ligand *via* the imine and one pyrazine nitrogen atom.

The 2,6-diisopropylphenyl group aligns with the 80.91° dihedral angle between the plane defined by the Cl₂PtN₂ fragment and the plane of benzene ring. The aromatic pyrazineimino fragment is not conjugated with the 2,6-diisopropylphenyl moiety because of the steric bulk of the isopropyl substituents.

The activity of the catalyst, Pt-1-POM where POM is H₅PV₂Mo₁₀O₄₀, was evaluated and optimized for the pinacol coupling reaction using benzaldehyde (neat, 2 mmol) as substrate, Pt-1 (0.01 mmol), POM (0.01–0.05 mmol) under 2 bar H₂ at 100 °C for 18 h, Fig. 2. The initial product, 1,2-diphenyl-1,2-ethanediol, of the coupling reaction was not observed. Instead, mostly due to the acidity of the polyoxometalate, further pinacol rearrangement (major route), deoxygenation or acetal formation occurred yielding the products shown in Scheme 3.

As can be observed from Fig. 2, at a 3 : 1 ratio of POM : Pt-1 a maximum conversion of the substrate of 86% was observed with a selectivity of 89% to the rearranged product, diphenylacetaldehyde. The conversion and product selectivity was strongly dependent on the ratio of Pt-1 to H₅PV₂Mo₁₀O₄₀; at ratios lower and higher than 1 : 3, the reaction conversion and selectivity was significantly diminished.

A series of control reactions led to the following results and conclusions. (i) There was a large synergetic effect when combining Pt-1 and H₅PV₂Mo₁₀O₄₀. Pt-1 (0.01 mmol) without POM showed only 5% conversion and POM (0.03 mmol) without Pt-1 showed

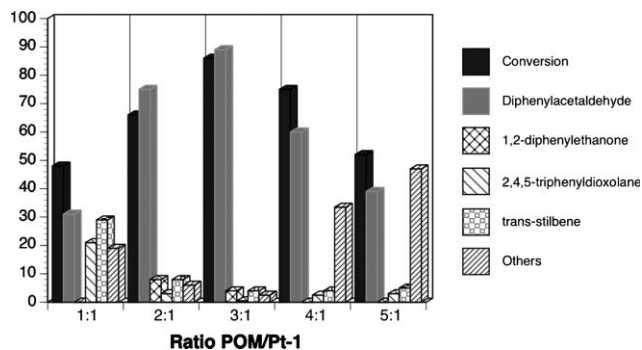
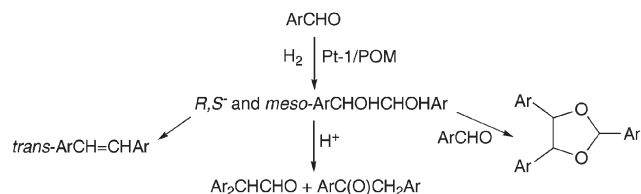


Fig. 2 Conversion and product selectivity in the pinacol coupling of benzaldehyde with hydrogen catalyzed by Pt-1-POM. Analysis was by GC (quantitative) and GC-MS (product identification).



Scheme 3 Formation of coupling products in Pt-1-POM catalyzed pinacol coupling reaction.

only 7% conversion; in both cases the selectivity to pinacol coupling was less than 20%. (ii) Replacing Pt-1 with analogous Pd-1 yielded almost exclusively reduction products (benzyl alcohol, toluene and some dibenzyl ether). (iii) Use of commercial 5 wt% Pd or 5 wt% Pt on carbon which was then impregnated with 5 wt% H₅PV₂Mo₁₀O₄₀ was ineffective for pinacol coupling; no coupling products with Pd/C and only 30% coupling products with Pt/C were observed. (iv) Use of H₃PW₁₂O₄₀ as a highly acidic but weakly oxidizing polyoxometalate in place of H₅PV₂Mo₁₀O₄₀ (acidic and strong oxidant) showed no synergetic effect to Pt-1, indicating that the role of the POM is indeed oxidation of H₂.

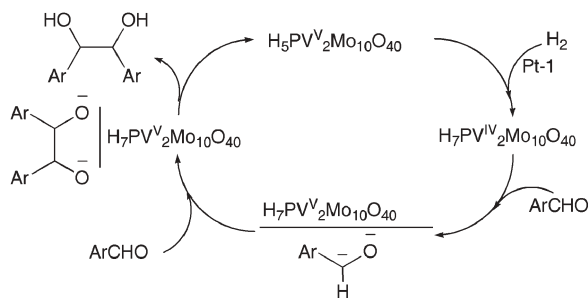
Using the optimized reaction conditions a series of benzaldehyde derivatives (2 mmol substrate, 0.01 mmol Pt-1, 0.03 mmol H₅PV₂Mo₁₀O₄₀, 2 bar H₂, 100 °C, 18 h) was reacted and evaluated. As one can see from the results in Table 1, the reaction conversions and yields of the rearranged products were generally high; the diphenylacetaldehyde derivatives were dominant in the product mixture. There was a tendency for reduced reactivity when the substituents were at the *ortho* positions to the carboxaldehyde that was also accompanied by more significant formation of 1,2-diarylethanone as reaction product. Inexplicably 4-chlorobenzaldehyde was significantly less reactive than 2-chlorobenzaldehyde. The formation of the deoxygenated stilbene products was relatively minor. Aliphatic aldehydes yielded mostly aldol condensation reaction products.

As noted above, the pinacol coupling reaction is thought to proceed *via* homo-radical or nucleophilic–electrophilic coupling reactions. To differentiate between these possibilities, less reactive 2,6-dichlorobenzaldehyde was used as co-substrate with more reactive benzaldehyde. The main product of this reaction was the cross-product, 2-(2,6-dichlorophenyl)-1-phenylethanone (90%

Table 1 Conversion and product selectivity in the pinacol coupling of benzaldehyde derivatives^a

Substituent	Conversion	Product selectivity		
		Ar ₂ CHCHO	ArCOCH ₂ Ar	ArCH=CHAr
H	84	86	4	4
4-MeO	82	83	0	12
2-MeO	91	89	0	6
4-Cl	9	89	11	0
2-Cl	70	46	20	23
4-Me	90	83	6	8
2-Me	98	87	5	8
2,4,6-Me	50	18	56	0
2,6-Cl	18	22	67	0
4- <i>i</i> -Pr	79	73	5	5

^a Reaction conditions: benzaldehyde derivative (2 mmol), Pt-1 (0.01 mmol), POM (0.03 mmol) under 2 bar H₂ at 100 °C for 18 h. Product selectivity is relative to all products. Analysis was by GC (quantitative) and GC-MS (product identification).



Scheme 4 Proposed reaction pathway for pinacol coupling.

selectivity). This suggests reaction of 2,6-dichlorobenzaldehyde with a benzaldehyde anion and not radical coupling, which would be expected to give mostly homo coupling of the more reactive benzaldehyde. Thus, a proposed mechanism for the pinacol coupling reaction catalyzed by Pt-1-POM is outlined in Scheme 4.

The hypothesis is that $H_5PV_2Mo_{10}O_{40}$ is reduced to $H_7PV_2Mo_{10}O_{40}$ by H_2 catalyzed by Pt-1,[§] followed by a two electron transfer (perhaps stepwise) to the aryl aldehyde to form the respective anion and the oxidized and protonated polyoxometalate. The bound aryl aldehyde anion is coupled with another aryl aldehyde substrate; the reaction is completed by proton transfer to yield the vicinal diol as initial product of the catalytic cycle.

We have demonstrated, apparently for the first time, a catalytic pinacol coupling reaction of aryl aldehydes using hydrogen as terminal reductant through use of a new hybrid metallorganic platinum–polyoxometalate catalyst. The acidic reaction conditions lead to further rearrangement and formation of diarylacetaldehyde as the major product in high yields.

This research was supported by the US-Israel Binational Science Foundation, the Israel Science Foundation, the Israel Ministry of Science and the Helen and Martin Kimmel Center for Molecular Design. R. N. is the Rebecca and Israel Sieff Professor of Organic Chemistry. Delina Barats is thanked for her help.

Notes and references

‡ Crystallographic data: empirical formula $C_{17}H_{21}N_3Cl_2Pt \cdot 1.5CHCl_3$; formula weight 713.42; crystal system triclinic $P\bar{1}$; $a = 11.1610(3)$ Å; $b = 15.0510(4)$ Å; $c = 15.2210$ Å; $\alpha = 98.9290(17)^\circ$; $\beta = 94.3500(16)^\circ$; $\gamma = 90.9850^\circ$. Data collection and refinement: Mo-K α ($\lambda = 0.71073$ Å) 49905 (11399 independent, $R_{int} = 0.046$) reflections; $\theta = 2.74$ – 27.42° ; $-14 \leq h \leq 14$, $-19 \leq k \leq 19$, $0 \leq l \leq 19$. Refinement of the data on 11399 unique reflections was with 524 parameters with 0 restraints. The goodness of fit on F^2 was 1.076. The final R indices for $I > 2\sigma(I)$ were $R_1 = 0.0280$ and $R_w = 0.0660$ and R indices for all data were $R_1 = 0.0366$ and $R_w = 0.0697$. CCDC 652837. For crystallographic data in CIF format see DOI: 10.1039/b710100g

§ The reduction of the polyoxometalate to the $H_7PV_2Mo_{10}O_{40}$ reduced species is easily observed by UV-vis spectroscopy and to the naked eye

through the formation of the well-known heteropoly blue with a broad absorption band centered around 650–700 nm. In this case quantitative analysis indeed showed the formation of $H_7PV_2Mo_{10}O_{40}$.

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