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A New Protocol to Synthesize Di(indolyl)pyrazolyl Methanes Using H_2PtCl_6 as a Catalyst in Ionic Liquid: Synthesis of Novel 3-[1*H*-indol-3-yl(3-phenyl-1*H*-pyrazol-4-yl)methyl]-1*H*-indoles

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Biologically important di(indolyl)pyrazolyl methanes and their derivatives were synthesized in excellent yields by the electrophilic substitution of indole with pyrazolyl aldehydes catalyzed by H_2PtCl_6 in ionic liquid.

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Introduction

Indole forms an integral part of many natural products of therapeutic importance and possesses potentially reactive sites for a variety of chemical reactions to generate molecular diversity. Bisindolylalkanes and their derivatives are found in bioactive metabolites of terrestrial and marine origin.[1] Several bis(indole)alkaloids, which exhibit biological activity including antibacterial, antiviral, and cytotoxic activities, have been isolated from the marine environment.[2] Streptindole is the first bacterial diindolylmethane metabolite possessing genotoxicity and DNA-damaging activities, which are reparable in *Bacillus subtilis* cells.[3] 3,3-Diindolylmethane has recently gained importance because of its potent anticarcinogenic properties.[4] There are reports where indole-based tripods have been synthesized through either condensation[5] of indole with triethyl orthoformate or by acylation[6] of indole with 2-alkyloxy-1,3-dioxolanes. Therefore, the synthesis of these moieties has become of interest to synthetic organic chemists and biologists. This manuscript describes efforts to synthesize indole-based tri(hetero)aryl methanes by exploiting the reactivity of indole.

A principle of green chemistry is to develop an alternative reaction medium, which is the basis for the development of many cleaner chemical technologies. Particularly, ionic liquids have recently gained recognition as possible environmentally safe alternatives to volatile organic solvents.[7] Further, use of ionic liquids, particularly in metal-catalyzed reactions, allows easy recovery and reuse of the catalysts.[8]

Lewis acids,[9] protic acids,[10] iodine,[11] clays,[12] and rare-earth perfluoroocanoates [$RE(PFO)_3$][13] promote these reactions. Recently, $ZrCl_4$ and SmI_3 were employed for this transformation.[14] However, many of these methods still suffer disadvantages such as long reaction time and use of too much catalyst which cannot be recycled. Therefore, a more efficient method to carry out this transformation is still sought. Recently, H_2PtCl_6 has received considerable attention as a mild catalyst for hydrosilylation and hydrogenation reactions.[15] Here, H_2PtCl_6 is introduced as a mild and highly efficient catalyst for the preparation of indole derivatives under mild conditions.

Results and Discussion

The experimental procedure is simple. Di(indolyl)pyrazolyl methanes have been synthesized by H_2PtCl_6/[bmim][Cl] catalyzed condensation of indole **1a**–**1e** and pyrazolyl aldehydes under mild conditions. Initially, the reaction of 1-methyl indole **1b** with pyrazolyl aldehyde **2a** was carried out in the presence of 2 mol% of H_2PtCl_6 as a catalyst in different solvents at room temperature. The reaction was carried out in the presence of HCl (2 mol%) and it was found the yield (30%) was low compared to when H_2PtCl_6 was used as a catalyst. The catalytic activity of H_2PtCl_6 was found to be high in [bmim][Cl]. The results are summarized in Table 1. All these ionic liquids gave the desired product in moderate to good yields (61–92%), among which [bmim][Cl] gave the best yield (92%). Because the reaction did not proceed to good extent in the presence of imidazole or *N*-methylimidazole in dichloromethane/ethanol (1/1), there is no role played by the Pt–imidazole complex in catalyzing the reaction. The catalyst was found to be only mildly effective in dichloromethane. The control reaction performed in the presence of [bmim][Cl] alone failed to yield the desired product. This result confirmed the efficiency of H_2PtCl_6 as a catalyst for the synthesis of di(indolyl)pyrazolyl methanes.

The method reported is favourable and gave good yields (89–94%). The maximum yield observed was 94% for **3g**. All the pyrazole aldehydes condensed with indoles to give di(indolyl)pyrazolyl methanes **3a**–**3j** in high yields (Scheme 1). The results are shown in Table 2.

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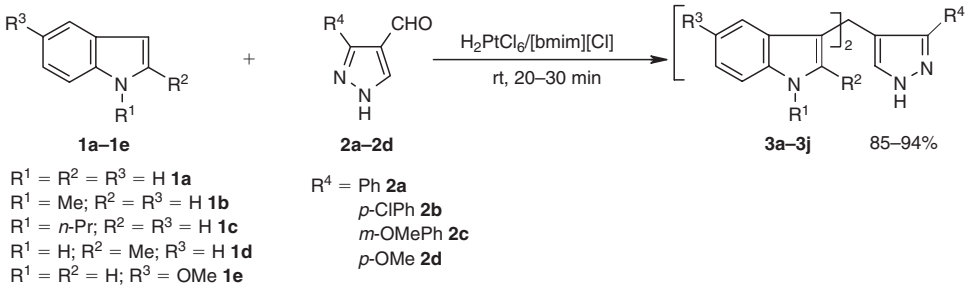


Scheme 1.

Table 1. Effect of solvent on the conversion to di(indolyl)pyrazolyl methane 3e

Entry	Solvents	Time [min]	Yield [%]
a	CH_2Cl_2	60	27
b	CH_3CN	30	63
c	EtOH	30	50
d	THF	60	47
e	[pmim][Br]	30	61
f	[ppy][Br]	30	36
g	[bmim][Cl]	30	92
h	[bpy][Cl]	30	90
i	[ppy][Cl]	30	87

Table 2. H_2PtCl_6/[bmim][Cl] catalyzed synthesis of di(indolyl)-pyrazolyl methanes

Entry	Substituents				Product	Time [min]	Yield [%]
	R^1	R^2	R^3	R^4			
a	H	H	H	Ph	**3a**	20	90
b	H	H	H	*p*-ClPh	**3b**	25	92
c	H	H	H	*m*-OMePh	**3c**	20	91
d	H	H	H	*p*-OMePh	**3d**	20	93
e	Me	H	H	Ph	**3e**	30	92
f	Me	H	H	*p*-ClPh	**3f**	30	85
g	Me	H	H	*m*-OMePh	**3g**	25	94
h	*n*-Pr	H	H	Ph	**3h**	30	89
i	H	Me	H	Ph	**3i**	25	90
j	H	H	OMe	Ph	**3j**	20	92

Table 3. H_2PtCl_6/[bmim][Cl] catalyzed synthesis of di(indolyl)-methanes

Entry	R^5		Product	Time [min]	Yield [%]
a	Ph	**4a**	**5a**[14]	10	91
b	*p*-OMePh	**4b**	**5b**[14]	20	95
c	2-furyl	**4c**	**5c**[14]	15	90
d	2-thiophenyl	**4d**	**5d**[14]	20	93
e	*n*-butyl	**4e**	**5e**[14]	15	89
f	3-indolyl	**4f**	**5f**[14]	30	89

The efficacy of Lewis acids such as $ZnCl_2$, $FeCl_3$, $InCl_3$, CuI, and $Sc(OTf)_3$ (2 mol%) in ionic liquid ([bmim][Cl]) was studied for the synthesis of **3a**. In comparison, H_2PtCl_6/[bmim][Cl] was found to be an excellent catalyst in terms of conversion and reaction time. Here, the H_2PtCl_6/[bmim][Cl] system is introduced as a catalyst for the synthesis of di(indolyl)pyrazolyl methanes under mild conditions. The simple heterocyclic aldehydes such as furfural and 2-thiophenecarbaldehyde also worked well without formation of side products Table 3. Indole-3-carbaldehyde reacted in the presence of a catalytic amount of H_2PtCl_6 to yield the trisindolyl methane **5f** in good yield (89%; Scheme 2).

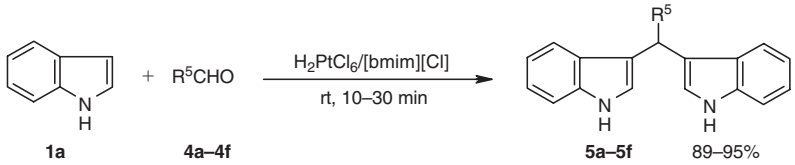
The remaining ionic liquid was thoroughly washed with ethyl acetate after completion of the reaction (monitored by TLC) and recycled in subsequent reactions. Second and third runs using recovered ionic liquid afforded similar yields to those obtained in the first run. In the fourth and fifth runs, the yields steadily decreased. However, the activity of ionic liquid was consistent and no decrease in yield was observed when the recycled ionic liquid was activated at 80°C under vacuum in each cycle. Experiments have been carried out to check the reusability of the ionic liquid on a single substrate only. Fresh ionic liquid was employed for each different entry in the tables.

Conclusions

H_2PtCl_6/[bmim][Cl] has been used for the first time as a novel and efficient catalyst for the synthesis of di(indolyl)pyrazolyl methanes by the electrophilic substitution reaction of indole with various aldehydes. The notable advantages of this procedure are the operational simplicity, fast and cleaner reaction profiles, and high yield, all of which make it an attractive strategy for the preparation of di(indolyl)pyrazolyl methanes. These di(indolyl)pyrazolyl methanes may show anticancer activity, which may be explored in further work.

Experimental

Melting points were recorded on a CONCORD melting point apparatus and are uncorrected. Analytical TLC was performed on precoated sheets of silica gel G 0.25 mm thick containing PF254 indicator (Merck, Darmstadt). H_2PtCl_6 was purchased from Aldrich chemicals and used as received. Ionic liquids were prepared according to reported procedures.[16] Column chromatography was performed with silica gel (100–200 mesh, s.d. fine). Mass spectra were recorded on JEOL-JMS DX 303HF mass spectrometer. IR spectra were recorded on a Perkin–Elmer FTIR spectrometer. NMR spectra were obtained on a JEOL ECA-500 MHz spectrometer. NMR spectra were recorded at 500 MHz in $CDCl_3$ and [D_6]DMSO, and the chemical shifts are given in ppm.



Scheme 2.

General Procedure

Synthesis of 1-Butyl-3-methylimidazolium Chloride [bmim][Cl]

1-Methylimidazole (25 g, 0.30 mol) was mixed with *n*-butyl chloride (42 g, 0.46 mol) and allowed to reflux for 24 h under nitrogen atmosphere. The excess *n*-butyl chloride was distilled off under reduced pressure and the residue was extracted thoroughly with diethyl ether (3 × 75 mL) to remove the unreacted starting materials. A clear yellow viscous oily liquid of 1-butyl-3-methylimidazolium chloride was obtained in 90% yield. The moisture content of the ionic liquid (0.06%) was determined by Karl–Fisher titration.

*Synthesis of 1-Methyl-3-[(1-methyl-1*H*-indol-3-yl) (3-Phenyl-1*H*-pyrazol-4-yl)methyl]-1*H*-indole* ***3e***

A mixture of 1-methylindole **1b** (200 mg, 1.53 mmol), 3-phenyl-1*H*-pyrazole-4-carbaldehyde **2a** (131 mg, 0.76 mmol), and H_2PtCl_6 (2 mol%) mixed with [bmim][Cl] (3 mL) was stirred at room temperature for 30 min. After complete conversion, as indicated by TLC, the mixture was extracted with ethyl acetate (3 × 20 mL). The ionic liquid was insoluble in ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4, concentrated and purified by column chromatography on silica gel (100–200 mesh, Merck, ethyl acetate/hexane (3/7)) to get pure brown solid **3e** in excellent yield (92%). Finally, the ionic liquid was heated to remove trace ethyl acetate, and recycled for subsequent reactions.

*3-[1*H*-Indol-3-yl(3-phenyl-1*H*-pyrazol-4-yl)methyl]-1*H*-indole* ***3a***

Light orange solid, mp 205–206°C. ν_{max} (KBr)/cm^{-1} 3410, 3048, 1627, 1462, 1420, 1339, 1095, 745. δ_H ([D$_6$]DMSO) 12.52 (1H, br s, pyrazole NH), 10.78 (2H, s, indole NH), 7.56 (2H, d, *J* 7.6), 7.44 (1H, s), 7.35–7.27 (5H, m), 7.17 (2H, d, *J* 7.6), 6.99 (2H, t, *J* 7.6), 6.86 (2H, s), 6.81 (2H, t, *J* 7.7), 5.83 (1H, s). δ_C ([D$_6$]DMSO) 170.9, 137.2, 134.3, 132.4, 129.2, 127.9, 126.8, 123.9, 121.4, 119.3, 118.8, 114.3, 112.1, 111.2, 56.6, 30.2. *m/z* 388 (M$^+$). (Found: C 80.38, H 5.16, N 14.40. $C_{26}H_{20}N_4$ requires C 80.39, H 5.19, N 14.42%.)

*3-[1*H*-Indol-3-yl(3-(4-chlorophenyl)-1*H*-pyrazol-4-yl)methyl]-1*H*-indole* ***3b***

Orange solid, mp 226–228°C. ν_{max} (KBr)/cm^{-1} 3417, 1623, 1454, 1416, 1099, 737. δ_H ([D$_6$]DMSO) 12.85 (1H, br s, pyrazole NH), 10.80 (2H, s, indole NH), 7.61 (2H, d, *J* 8.2), 7.39 (3H, t, *J* 7.6), 7.35 (1H, t, *J* 7.6), 7.34 (1H, s), 7.22 (2H, d, *J* 8.0), 7.03 (2H, t, *J* 7.7), 6.88 (2H, s), 6.85 (2H, t, *J* 7.6), 5.86 (1H, s). δ_C ([D$_6$]DMSO) 160.1, 137.2, 134.4, 128.7, 126.6, 126.2, 124.0, 121.1, 119.5, 118.5, 116.6, 116.1, 115.9, 111.8, 109.2, 33.5. *m/z* 422 (M$^+$). (Found: C 73.80, H 4.53, N 13.19. $C_{26}H_{19}ClN_4$ requires C 73.84, H 4.53, N 13.25%.)

*3-[1*H*-Indol-3-yl(3-(3-methoxyphenyl)-1*H*-pyrazol-4-yl)methyl]-1*H*-indole* ***3c***

Orange solid, mp 202–204°C. ν_{max} (KBr)/cm^{-1} 3418, 3037, 1620, 1462, 1431, 1250, 1088, 1037, 745. δ_H ([D$_6$]DMSO) 12.80 (1H, br s, pyrazole NH), 10.76 (2H, s, indole NH), 7.31 (2H, d, *J* 8.4), 7.27 (1H, s), 7.24–7.17 (4H, m), 7.03 (1H, s, Ph), 7.00 (3H, t, *J* 7.7), 6.85 (2H, s), 6.81 (2H, t, *J* 7.6), 5.83 (1H, s), 3.37 (3H, s). δ_C ([D$_6$]DMSO) 159.7, 137.2, 130.1, 129.4, 126.9, 125.3, 123.9, 122.0, 121.4, 119.9, 119.4, 119.1, 118.7, 116.2, 114.0, 112.6, 112.0, 55.0, 30.4. *m/z* 418 (M$^+$). (Found: C 77.45, H 5.32, N 13.36. $C_{27}H_{22}N_4O$ requires C 77.49, H 5.30, N 13.39%.)

*3-[1*H*-Indol-3-yl(3-(4-methoxyphenyl)-1*H*-pyrazol-4-yl)methyl]-1*H*-indole* ***3d***

Brown solid, mp 207–209°C. ν_{max} (KBr)/cm^{-1} 3414, 3034, 1612, 1427, 1415, 1338, 1238, 1088, 1018, 745. δ_H ([D$_6$]DMSO) 12.83 (1H, br s, pyrazole NH), 10.80 (2H, s, indole NH), 7.50 (2H, d, *J* 8.0), 7.42 (1H, s), 7.32 (2H, t, *J* 7.6), 7.20 (2H, d, *J* 7.7), 7.02 (2H, t, *J* 7.6), 6.91 (2H, t, *J* 7.6), 6.88 (2H, s), 6.85 (2H, t, *J* 7.7), 5.83 (1H, s), 3.73 (3H, s). δ_C ([D$_6$]DMSO) 162.8, 159.1, 137.2, 130.2, 128.9, 126.9, 123.8, 121.3, 119.4, 119.2, 118.6, 114.5, 112.5, 111.9, 110.0, 55.5, 30.2. *m/z* 418 (M$^+$). (Found: C 77.46, H 5.28, N 13.41. $C_{27}H_{22}N_4O$ requires C 77.49, H 5.30, N 13.39%.)

*1-Methyl-3-[(1-methyl-1*H*-indol-3-yl) (3-Phenyl-1*H*-pyrazol-4-yl)methyl]-1*H*-indole* ***3e***

Brown solid, mp 142°C. ν_{max} (KBr)/cm^{-1} 3432, 3059, 2926, 1616, 1473, 1329, 1097, 1013, 740. δ_H ([D$_6$]DMSO) 12.84 (1H, br s, pyrazole NH), 7.55 (2H, d, *J* 8.4), 7.35 (2H, d, *J* 8.5), 7.33 (3H, d, *J* 3.9), 7.31 (1H, s), 7.18 (2H, d, *J* 7.6), 7.05 (2H, t, *J* 7.6), 6.85 (2H, t, *J* 7.6), 6.83 (2H, s), 5.80 (1H, s), 3.64 (6H, s). δ_C ([D$_6$]DMSO) 164.2, 149.4, 137.6, 132.2, 129.4, 129.1, 128.3, 127.1, 122.1, 121.5, 119.5, 118.9, 118.2, 116.5, 110.2, 32.8, 29.9. *m/z* 416 (M$^+$). (Found: C 80.72, H 5.78, N 13.44. $C_{28}H_{24}N_4$ requires C 80.74, H 5.81, N 13.45%.)

*1-Methyl-3-[(1-methyl-1*H*-indol-3-yl) (3-(4-Chlorophenyl)-1*H*-pyrazol-4-yl)methyl]-1*H*-indole* ***3f***

Pale orange solid, mp 138°C. ν_{max} (KBr)/cm^{-1} 3431, 3056, 2928, 1617, 1470, 1326, 1097, 745. δ_H ([D$_6$]DMSO) 12.85 (1H, br s, pyrazole NH), 7.54 (2H, d, *J* 8.4), 7.35 (2H, d, *J* 8.5), 7.33 (2H, d, *J* 7.6), 7.31 (1H, s), 7.18 (2H, d, *J* 8.5), 7.05 (2H, t, *J* 7.7), 6.85 (2H, t, *J* 7.6), 6.82 (2H, s), 5.79 (1H, s), 3.64 (6H, s). δ_C ([D$_6$]DMSO) 161.5, 152.1, 129.4, 129.1, 128.3, 127.1, 122.1, 121.5, 119.5, 118.9, 118.2, 117.1, 115.2, 111.1, 110.2, 89.7, 32.1. *m/z* 450 (M$^+$). (Found: C 74.56, H 5.11, N 12.39. $C_{28}H_{23}ClN_4$ requires C 74.57, H 5.14, N 12.42%.)

*1-Methyl-3-[(1-methyl-1*H*-indol-3-yl) (3-(3-Methoxyphenyl)-1*H*-pyrazol-4-yl)methyl]-1*H*-indole* ***3g***

Pale orange solid, mp 172–174°C. ν_{max} (KBr)/cm^{-1} 3430, 2923, 1454, 1416, 1037, 742. δ_H ([D$_6$]DMSO) 12.85 (1H, br s, pyrazole NH), 7.48 (2H, d, *J* 8.4), 7.39 (1H, s), 7.36 (3H, t, *J* 6.1), 7.34 (1H, s), 7.26 (2H, t, *J* 6.9), 7.04 (2H, t, *J* 6.9), 6.73 (2H, d, *J* 8.4), 6.68 (2H, s), 5.95 (1H, s), 3.70 (6H, s). δ_C ([D$_6$]DMSO) 171.5, 159.4, 143.7, 137.7, 136.0, 129.2, 128.2, 127.3, 124.4, 121.5, 120.2, 118.8, 118.7, 114.2, 109.2, 60.6, 55.3, 32.8, 29.9. *m/z* 446 (M$^+$). (Found: C 78.02, H 5.83, N 12.49. $C_{29}H_{26}N_4O$ requires C 78.00, H 5.87, N 12.55%.)

*1-Propyl-3-[(1-propyl-1*H*-indol-3-yl) (3-Phenyl-1*H*-pyrazol-4-yl)methyl]-1*H*-indole* ***3h***

Pale brown solid, mp 208–210°C. ν_{max} (KBr)/cm^{-1} 3415, 3032, 1620, 1430, 1088, 1035, 745. δ_H ([D$_6$]DMSO) 12.82 (1H, br s, pyrazole NH), 7.56 (2H, d, *J* 7.6), 7.35–7.32 (5H, m), 7.28 (1H, s), 7.24 (2H, t, *J* 7.7), 7.19 (2H, t, *J* 7.7), 6.97 (2H, t, *J* 7.7), 6.68 (2H, s), 5.94 (1H, s), 4.01–3.97 (4H, m), 1.83–1.73 (4H, m), 0.85 (6H, t, *J* 6.9). δ_C ([D$_6$]DMSO) 144.3, 137.0, 131.9, 128.7, 127.9, 127.8, 127.4, 127.3, 122.1, 121.3, 120.3, 118.6, 118.2, 109.4, 47.9, 30.1, 27.1, 23.6, 11.6.

m/z 472 (M^+). (Found: C 81.27, H 6.80, N 11.86. $C_{32}H_{32}N_4$ requires C 81.32, H 6.82, N 11.85%.)

*2-Methyl-3-[(2-methyl-1*H*-indol-3-yl) (3-Phenyl-1*H*-pyrazol-4-yl)methyl]-1*H*-indole* ***3i***

Brownish orange solid, mp 194–196°C. ν_{max} (KBr)/cm^{-1} 3422, 3298, 1656, 1472, 1113, 1042, 756. δ_H ([D_6]DMSO) 12.75 (1H, br s, pyrazole NH), 10.64 (2H, s, indole NH), 7.50 (2H, d, *J* 7.6), 7.23 (3H, t, *J* 6.9), 7.17 (2H, d, *J* 7.6), 7.14 (1H, s), 6.92 (2H, d, *J* 7.6), 6.86 (2H, t, *J* 7.6), 6.68 (2H, t, *J* 7.6), 5.78 (1H, s), 2.04 (6H, s). δ_C ([D_6]DMSO) 170.8, 160.9, 135.5, 131.9, 128.9, 128.6, 127.3, 121.5, 120.1, 118.7, 118.5, 113.4, 112.5, 111.8, 110.9, 60.3, 30.3. *m/z* 416 (M^+). (Found: C 80.71, H 5.80, N 13.42. $C_{28}H_{24}N_4$ requires C 80.74, H 5.81, N 13.45%.)

*5-Methoxy-3-[(5-methoxy-1*H*-indol-3-yl) (3-Phenyl-1*H*-pyrazol-4-yl)methyl]-1*H*-indole* ***3j***

Orange solid, mp 118–120°C. ν_{max} (KBr)/cm^{-1} 3417, 3300, 1620, 1482, 1211, 1054, 772. δ_H ([D_6]DMSO) 12.70 (1H, br s, pyrazole NH), 10.59 (2H, s, indole NH), 7.54 (2H, d, *J* 7.6), 7.34 (2H, t, *J* 6.9), 7.27 (1H, t, *J* 7.6), 7.21 (1H, s), 7.19 (2H, s), 6.85 (2H, s), 6.65 (2H, dd, *J* 2.3, 8.4), 6.57 (2H, s), 5.67 (1H, s), 3.51 (6H, s). δ_C ([D_6]DMSO) 170.5, 153.1, 135.6, 130.6, 130.0, 129.4, 129.1, 127.9, 127.3, 124.5, 121.6, 118.7, 112.6, 111.0, 101.6, 55.7, 30.3. *m/z* 448 (M^+). (Found: C 74.94, H 5.33, N 12.48. $C_{28}H_{24}N_4O_2$ requires C 74.98, H 5.39, N 12.49%.)

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