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Efficient and versatile catalysis of N-alkylation of heterocyclic amines with alcohols and one-pot synthesis of 2-aryl substituted benzazoles with newly designed ruthenium(II) complexes of PNS thiosemicarbazones†

Rangasamy Ramachandran,[a] Govindan Prakash,[a] Sellappan Selvamurugan,[a] Periasamy Viswanathamurthi,*[a] Jan Grzegorz Malecki[b] and Venkatachalam Ramkumar[c]

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Ruthenium(II) carbonyl complexes with phosphine-functionalized **PNS** type thiosemicarbazone ligands [RuCl(CO)(EPh_3)(**L**)] (**1–6**) (E = P or As, **L** = 2-(2-(diphenylphosphino)benzylidene) thiosemicarbazone (**PNS-H**), 2-(2-(diphenylphosphino)benzylidene)-*N*-methylthiosemicarbazone **(PNS-Me)**, 2-(2-(diphenylphosphino)benzylidene)-*N*-phenylthiosemicarbazone (**PNS-Ph**)) have been synthesized and characterized by elemental analysis and spectroscopy (IR, UV-Vis, ^{1}H, ^{13}C, ^{31}P-NMR) as well as ESI mass spectrometry. The molecular structures of complexes **1**, **2** and **6** were identified by means of single-crystal X-ray diffraction analysis. The analysis revealed that all the complexes possess a distorted octahedral geometry with the ligand coordinating in a uni-negative tridentate **PNS** fashion. All the ruthenium complexes (**1–6**) were tested as catalyst for N-alkylation of heteroaromatic amines with alcohols. Notably, complex **2** was found to be a very efficient and versatile catalyst towards N-alkylation of a wide range of heterocyclic amines with alcohols. Complex **2** can also catalyze the direct amination of 2-nitropyridine with benzyl alcohol to the corresponding secondary amine. Furthermore, a preliminary examination of performance for N,N-dialkylation of diamine showed promising results, giving good conversion and high selectivity. In addition, N-alkylation of *ortho*-substituted anilines (–NH_2, –OH and –SH) led to the one-pot synthesis of 2-aryl substituted benzimidazoles, benzoxazoles and benzothiazoles, also revealing the catalytic activity of complex **2**.

Introduction

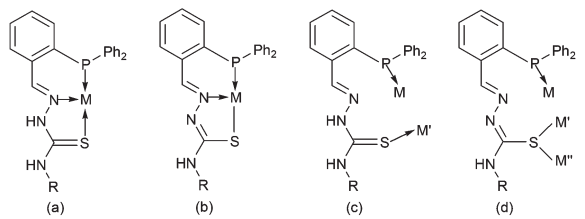
The nature of the multidentate ligand has a profound effect on the coordination chemistry of a metal complex, and so the design and "tailoring" of ligand properties can lead to innovative metal chemistry.[1] Special attention has been directed to the use of multidentate thiosemicarbazone ligands having both hard and soft donor atoms (*e.g.* N_2S_2 or XNS, X = N, O, S and P), because of their coordination versatility[2] and remarkable applications in catalytic[3] and biological sciences.[4] Thiosemicarbazones functionalized with an additional donor group have become important ligands due to the potential hemilability of the new donor group, which can play a dual role in a catalyst since they can easily enable coordination sites and, at the same time, protect the coordination sites by a dynamic "on and off" chelating effect.[5]

Several donor groups have been reported to functionalize thiosemicarbazones, their complexes exhibit high activity when used as a catalyst in Pd-catalyzed Suzuki–Miyaura cross coupling,[6] Heck or Buchwald–Hartwig amination reactions.[7] More recently, ruthenium mediated N-alkylation and transfer hydrogenations have also appeared in the literature.[8] We have a continuing broad interest in thiosemicarbazone ligand systems containing diphenylphosphino pendant functional-

[a]*Department of Chemistry, Periyar University, Salem-636 011, India. E-mail: viswanathamurthi72@gmail.com; Fax: +91 427 2345124*
[b]*Department of Crystallography, Silsian University, Szkolna 9, 40-006 Katowice, Poland*
[c]*Department of Chemistry, Indian Institute of Technology Madras, Chennai 600 036, India*

†Electronic supplementary information (ESI) available: ^{1}H and ^{13}C-NMR spectrum of ligands (PNS-H, PNS-Me, PNS-Ph) and complexes (**1–6**), ^{31}P-NMR and ESI-MS spectrum of complexes (**1–6**), general experimental procedures and characterization data for N-alkylated products. CCDC 969003–969005. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4dt00006d

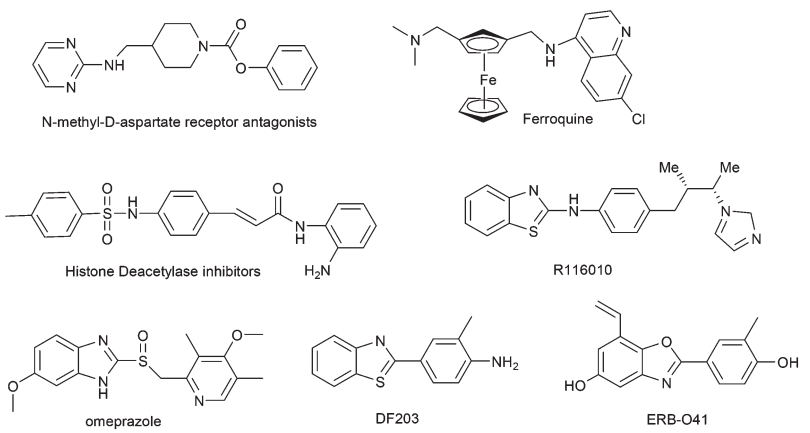
ities that can potentially form stable complexes with metal ions. Since the first synthesis, performed by Brceski and co-workers,[9] phosphino-thiosemicarbazone ligands have been widely used in catalysis. With the simultaneous presence of soft P, S and hard N donors, the phosphino-thiosemicarbazone ligands exhibit various coordination modes (Scheme 1): (a) neutral tridentate (P, N and S bonded to M),[10] (b) monoanionic tridentate (P, N and deprotonated S bonded to M),[11] (c) neutral bidentate (P and S bonded to M)[12] and (d) monoanionic bridging ligand (P bonded to M and S bonded to M′).[13] Coordination through neutral bidentate and monoanionic bridging PNS ligands is found in some Au(I) and Ag(I) complexes.[13,14] It has been suggested that intramolecular hydrogen bonding exists between the terminal thioamide nitrogen atoms as donors and the imine nitrogen atoms as acceptors. The PNS ligands, which do not form an intramolecular hydrogen bond, tend to coordinate predominately in a neutral or monoanionic tridentate PNS fashion. Examples of this type of coordination are rare and so far only known for complexes with Cu(I) and Au(II).[11,15] This variable mode of binding of phosphino-thiosemicarbazone has encouraged us to explore its coordination chemistry further, and herein we have chosen ruthenium as the metal center to interact with the thiosemicarbazone. One reason behind the choice of this particular metal center is its ability to take up different coordination environments with salicylaldehyde/napthaldehyde thiosemicarbazones which have been reported recently,[16] which makes its coordination chemistry very interesting.



Scheme 1 Different coordination modes of the triphenyl phosphine-functionalized thiosemicarbazone ligands in various metal complexes.

Amines are key building blocks in industrial and medicinal chemistry today.[17] Traditionally, these compounds are synthesized by alkylation of primary amines with good leaving groups such as alkyl halides, tosylates, mesylates and triflates.[18] However, the procedure frequently leads to overalkylation and, considering the necessity for environmentally friendly processes, the high toxicity of many alkylating agents is a major drawback, especially in pharmaceutical, biochemical and industrial applications. Nevertheless, the use of transition metal complexes as catalysts *via* a borrowing-hydrogen methodology makes N-alkylation using alcohols a potentially less hazardous and more atom-economical process.[19–24] While both heterogeneous and homogeneous catalysts have been known to promote the reaction,[19b] iridium[20] and ruthenium[21–23] complexes have constituted a vast majority of the homogeneous catalysts because of their high catalytic performance with high product selectivity. Several iridium and ruthenium catalytic systems bearing phosphine ligands have been reported to complete the N-alkylation of amines with alcohols in good yields and selectivity.[24]

Pyrimidine, ferrocene and sulfonamide are currently considered to be privileged scaffolds and have gained remarkable popularity in the fields of bioorganic and medicinal chemistry.[25] In particular, 2-(*N*-alkylamino)pyrimidines, 2-(*N*-alkylamino)ferrocene and 2-(*N*-alkylamino)sulfonamides exhibit a wide range of biological properties. Selective examples are *N*-methyl-D-aspartate receptor antagonists, ferroquine and histone deacetylase inhibitors.[26] Bioactive molecules possessing 2-(*N*-alkylamino)benzothiazole core, such as R116010 (II) and riluzole(I) can act as potent inhibitor of retinoic acid metabolism, glutamate neurotransmitter and *N*-myristoyltransferase (Nmr) inhibitor.[27] In addition, benzazoles such as benzimidazoles, benzoxazoles and benzothiazoles are important structural motifs in pharmaceuticals,[28] which involve nearly one-quarter of the top 100 selling drugs including DF203, ERB-O41 and omeprazole (Scheme 2).[29] Development of general methods for the synthesis of these heterocyclic compounds is thus highly relevant for drug discovery.



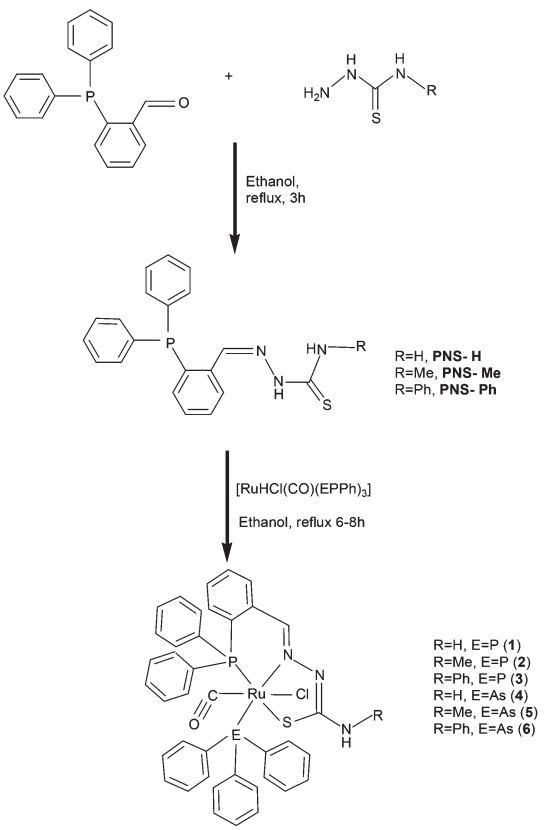
Scheme 2 Bioactive molecules with pyrimidine, ferrocene, sulfonamide, 2-*N*-(alkylaminoazole) and benzazole moieties.

In view of the above and as a part of our ongoing research work,[8a,16a,30] we report herein a series of ruthenium(II) carbonyl complexes bearing phosphino-thiosemicarbazone ligands and investigate the role of terminal substitution of ligands and co-ligands in determining catalytic activity for N-alkylation of amines and one-pot synthesis of 2-aryl substituted benzimidazoles, benzoxazoles and benzothiazoles. The attractive features of these reactions include the use of low toxic organic materials, excellent atom economy, water as the only byproduct and high selectivity towards the products.

Results and discussion

Catalyst design

In designing Ru complexes (**1–6**) (Scheme 3), we were interested in probing the role of catalysis of terminal *N*-substitution in phosphino-thiosemicarbazones (**PNS-H**, **PNS-Me** and **PNS-Ph**), co-ligands, and the resulting differences in the structure of the complexes (**1–6**). The ruthenium(II) complexes (**1–6**) are closely related, only differing by H *versus* Me or Ph in the terminal *N*-substituent and P or As in coligands. The ligand precursors **PNS-H**, **PNS-Me** and **PNS-Ph** (Scheme 3) were synthesized by condensation of 2-diphenylphosphinebenzaldehyde with thiosemicarbazide, 4-*N*-methylthiosemicarbazide and 4-*N*-phenylthiosemicarbazide, respectively, following the published procedure.[9–15] The new Ru catalysts of the type



Scheme 3 Synthesis of the ruthenium(II) complexes.

[RuCl(CO)(EPh$_3$)(**L**)] (**1–6**) were synthesized by reacting **PNS-H**, **PNS-Me** and **PNS-Ph** with one equivalent of [RuHCl(CO)(EPPh$_3$)$_3$] in ethanol under reflux for 6–8 h (see Scheme 3 for further details). These Ru complexes are air stable, were obtained in good yield (73–82%), and were characterized by analytical, spectroscopic methods (IR, UV-Vis, ^{1}H, ^{13}C, ^{31}P-NMR and ESI-MS) (Fig. S1–S30, ESI†) and by X-ray crystallography for **1**, **2** and **6** as described further below. The analytical data of the complexes agreed well with the proposed molecular formulae.

Spectroscopic studies

The IR spectra of the ligands and the corresponding ruthenium(II) complexes provided significant information about the metal–ligand bonding. A strong vibration observed at 1546–1541 cm^{-1} in the ligands corresponding to $\nu_{C=N}$ was shifted to 1592–1582 cm^{-1} in all the complexes indicating the participation of azomethine nitrogen in bonding.[15] A sharp band observed at 760–758 cm^{-1}, ascribed to $\nu_{C=S}$ in the ligands, has completely disappeared in the spectra of all the new Ru complexes, and the appearance of a new band at 747–738 cm^{-1} due to ν_{C-S} indicated the coordination of the sulfur atom after enolisation followed by deprotonation.[16a] All the complexes display a medium to strong band in the region 1962–1945 cm^{-1}, which is attributed to the terminally coordinated carbonyl group (C≡O) and is observed at a slightly higher frequency than in the precursor complexes.[16b] In addition, vibrations corresponding to the presence of PPh$_3$/AsPh$_3$ also appeared in the expected region. The electronic spectra of the complexes (**1–6**) have been recorded in dichloromethane and they displayed four bands in the region around 231–435 nm. The high-energy absorption shoulder in the region 231–258 nm has been assigned to ligand-centered (LC) transitions,[31] the lowest energy shoulder observed in the region 343–369 nm has been attributed to the ligand to metal charge transfer (LMCT) transitions, and the band 427–435 nm has been assigned to a forbidden (d→d) transition.

The ^{1}H NMR spectra of the ligands and their complexes (**1–6**) show the signals in the expected regions (Fig. S1–S9, ESI†). The singlets that appeared for the N–NH–C=S proton of the free ligands at 11.94–11.52 ppm are absent in the complexes, supporting the enolization and coordination of the thiolate sulfur to the Ru(II) ion. The doublet due to azomethine proton (8.86–8.73 ppm) in the complexes are slightly downfield compared to the free ligands (8.79–8.65 ppm), suggesting deshielding upon coordination to the Ru(II) ion. The spectra of the complexes showed a singlet at 8.60–8.15 ppm, which has been assigned to NH$_2$ or NH-R protons. Further, the spectra of all the complexes showed a series of signals for aromatic protons at 7.88–6.51 ppm. In addition, a singlet appeared around 1.22 ppm for complexes **2** and **5** corresponding to the terminal –CH$_3$ group protons.

The ^{13}C NMR spectra show the expected signals in the appropriate regions (Fig. S10–S18, ESI†). For the uncoordinated ligands, the C=N and C=S signals appear in the regions around 141.50–140.64 ppm and 178.93–175.81 ppm. Upon coordination and formation of the new Ru complexes, a

downfield shift is observed for the signals of the C=N (around 5 ppm), while the C=S carbon atom signals appeared in the upfield region between 176.45 and 176.03 ppm. This is consistent with the P, N, S coordination and thioenolization of the C=S of thiosemicarbazone moieties. In complexes (**1–6**), aromatic carbon atoms of the phenyl group observed around 138.91–115.83 ppm are comparable to the literature values.[32] The C≡O carbon resonating at 206.73–206.02 ppm is comparable with earlier observations.[33] In addition, a signal appeared around 31.17–30.60 ppm for complexes **2** and **5** corresponding to the terminal methyl group carbon.

The presence of a residual PPh_3 coordinated to Ru(II) (**1–3**) is confirmed by ^{31}P NMR (Fig. S19–S24, ESI†), where two doublets are observed respectively at 30.15–29.79 ppm (J_{pp} = 22.6 Hz, PPh_3) and 28.85–28.74 ppm (J_{pp} = 24.2 Hz, PPh_2). These values for coupling constants suggest a *cis* disposition between the phosphorus nuclei, as already reported for other Ru(II) phosphine complexes.[34] The singlet observed at 32.73–31.38 ppm in complexes **4**, **5** and **6**, respectively, suggested the presence of the PPh_2 group in the thiosemicarbazone moieties. ESI-mass spectra of the complexes (**1–6**) generally show the molecular ion peak with the loss of a chloride ion (Fig. S25–S30, ESI†).

Structural studies

Even though the analytical and spectral data gave some idea about the molecular formulae of the complexes, they do not indicate the exact coordination of phosphino-thiosemicarbazone units in them. Hence, there is a need to prove their structures by X-ray crystallography. The crystal data and structure refinement parameters for complexes **1**, **2** and **6** are summarized in Table 1 and selected bond lengths and bond angles are depicted in Table 2. The ORTEP view of complexes **1**, **2** and **6** along with the atomic numbering scheme are given in Fig. 1–3. The single-crystal X-ray studies revealed that complexes **1** and **2** are crystallized in a monoclinic system with the space group $P2_1/c$, whereas complex **6** crystallized in a triclinic system with the space group $P\bar{1}$. The coordination geometry around the Ru(II) ion is a slightly distorted octahedron, where the basal plane is constructed of a phosphorus atom, the imine nitrogen and the thiolate sulfur atom of the ligand in a mononegative tridentate PNS fashion, and a triphenylphosphine/triphenylarsine. The remaining apical coordination sites are filled up by a chlorine atom and a carbonyl group. The chloride and carbonyl ligands of complexes **1** and **2** are disordered in two orientations with the ratio 51 : 49 for **1** and 55 : 45 for **2**, respectively.[35a,b] In complexes **1**, **2** and **6** the coordination sphere is the same and the general structural motifs differ only in the terminal substitution (R = H, Me, Ph). Thus the structure of one of the Ru(II) complexes **1** (Fig. 1) will be described in detail here.

The tridentate PNS chelate ligand coordinated equatorially to the metal ion with the formation of one six-membered ring and another five membered ring with the bite angles of

Table 1 Crystal data and structure refinement parameters for complexes **1**, **2** and **6**

	1	**2**	**6**
CCDC number	969003	969004	969005
Empirical formula	$C_{39}H_{32}ClN_3OP_2RuS{\cdot}0.5(C_2H_8O_2)$	$C_{40}H_{34}ClN_3OP_2RuS$	$C_{45}H_{36}AsClN_3OPRuS$
Formula weight	821.24	803.22	909.24
T (K)	295	298	295
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$
Unit cell dimensions			
a (Å)	14.3822(5)	14.3388(8)	10.2991(8)
b (Å)	16.6752(6)	16.6137(6)	13.1254(11)
c (Å)	15.1543(4)	15.0818(8)	15.2952(13)
α (°)	90.00	90.00	97.686(7)
β (°)	96.312(3)	96.268(4)	94.380(7)
γ (°)	90.00	90.00	96.521(7)
Volume (Å^3)	3612.4(2)	3571.3(3)	2027.0(3)
Z	4	4	2
Density (calculated) (Mg m^{-3})	1.510	1.494	1.490
Absorption coefficient (mm^{-1})	0.695	0.699	1.392
F(000)	1680	1640	920
Scan range for data collection (°)	3.42 to 25.05	1.83 to 24.99	3.62 to 28.70
Index ranges	$-17 \le h \le 17$	$-17 \le h \le 17$	$-12 \le h \le 12$
	$-19 \le k \le 18$	$-19 \le k \le 18$	$-15 \le k \le 15$
	$-17 \le l \le 18$	$-17 \le l \le 17$	$-16 \le l \le 18$
Reflections collected/unique, R_{int}	18 987/6367, 0.0353	40 742/6289, 0.1379	14 624/7165, 0.0673
Completeness to theta$_{max}$	0.997	0.994	0.996
Data/restraints/parameters	6367/0/486	6289/0/382	7165/0/487
Goodness-of-fit on F^2	1.060	0.994	1.070
Final R indices $[I > 2\sigma(I)]^a$	R_1 = 0.035, wR_2 = 0.081	R_1 = 0.056, wR_2 = 0.101	R_1 = 0.056, wR_2 = 0.114
R indices (all data)	R_1 = 0.047, wR_2 = 0.086	R_1 = 0.093, wR_2 = 0.111	R_1 = 0.076, wR_2 = 0.122

[a] Structures were refined on F_o^2: $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$, where $w^{-1} = [\sum(F_o^2) + (aP)^2 + bP]$ and $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

Table 2 Selected geometrical parameters for complexes **1**, **2** and **6**

1		**2**		**6**	
Interatomic distances (Å)					
Ru(1)–C(1A)[a]	1.88(2)	Ru(1)–C(41)[a]	1.8183	Ru(1)–C(1)	1.89(3)
Ru(1)–C(1B)[a]	1.809(18)	Ru(1)–C(41A)[a]	1.8384	—	—
Ru(1)–N(1)	2.125(3)	Ru(1)–N(1)	2.128(4)	Ru(1)–N(1)	2.02(2)
Ru(1)–P(1)	2.344(8)	Ru(1)–P(1)	2.3429	Ru(1)–P(1)	2.333(8)
Ru(1)–S(1)	2.386(8)	Ru(1)–S(1)	2.3882	Ru(1)–S(1)	2.393(8)
Ru(1)–P(2)	2.398(8)	Ru(1)–P(2)	2.3929	Ru(1)–As(1)	2.469(4)
Ru(1)–Cl(1)[a]	2.441(4)	Ru(1)–Cl(1)[a]	2.4181	Ru(1)–Cl(1)	2.425(9)
Ru(1)–Cl(2)[a]	2.397(5)	Ru(1)–Cl(1A)[a]	2.4478	—	—
Bond angles (°)					
C(1B)–Ru(1)–N(1)	87.4(6)	C(41)–Ru(1)–P(1)	91.3	C(1)–Ru(1)–N(1)	89.6(10)
C(1B)–Ru(1)–P(1)	91.1(6)	C(41)–Ru(1)–S(1)	89.3	C(1)–Ru(1)–P(1)	92.4(8)
C(1B)–Ru(1)–S(1)	90.2(6)	C(41)–Ru(1)–P(2)	90.3	C(1)–Ru(1)–S(1)	91.3(8)
C(1B)–Ru(1)–P(2)	90.2(6)	C(41)–Ru(1)–Cl(1A)[a]	168.9	C(1)–Ru(1)–Cl(1)	174.5(8)
C(1B)–Ru(1)–Cl(1)[a]	166.6(6)	N(1)–Ru(1)–C(41)	87.01(11)	C(1)–Ru(1)–As(1)	88.5(8)
C(1B)–Ru(1)–Cl(2)[a]	173.7(5)	C(41A)–Ru(1)–Cl(1)[a]	169.6	—	—
N(1)–Ru(1)–P(1)	90.63(7)	N(1)–Ru(1)–P(1)	91.04(11)	N(1)–Ru(1)–P(1)	92.0(6)
N(1)–Ru(1)–S(1)	81.21(7)	N(1)–Ru(1)–S(1)	81.15(11)	N(1)–Ru(1)–S(1)	79.0(6)
N(1)–Ru(1)–P(2)	169.37(7)	N(1)–Ru(1)–P(2)	168.74(11)	N(1)–Ru(1)–Cl(1)	85.0(7)
N(1)–Ru(1)–Cl(1)	79.29(16)	N(1)–Ru(1)–Cl(1)	85.08(11)	N(1)–Ru(1)–As(1)	166.3(6)
P(1)–Ru(1)–S(1)	171.67(3)	P(1)–Ru(1)–S(1)	172.1	P(1)–Ru(1)–S(1)	170.2(3)
P(1)–Ru(1)–P(2)	99.78(3)	P(1)–Ru(1)–P(2)	100.0	P(1)–Ru(1)–Cl(1)	86.9(3)
P(1)–Ru(1)–Cl(1)	87.63(8)	P(1)–Ru(1)–Cl(1)	91.8	P(1)–Ru(1)–As(1)	101.7(2)
S(1)–Ru(1)–P(2)	88.45(3)	S(1)–Ru(1)–P(2)	87.9	S(1)–Ru(1)–Cl(1)	88.6(3)
S(1)–Ru(1)–Cl(1)	89.22(8)	S(1)–Ru(1)–Cl(1)	88.6	S(1)–Ru(1)–As(1)	87.5(2)
P(2)–Ru(1)–Cl(1)	103.15(14)	P(2)–Ru(1)–Cl(1)	92.1	Cl(1)–Ru(1)–As(1)	97.0(2)

[a] The molecular structures **1** and **2** show a disorder in which the Cl ligand and CO ligand have two orientations in the ratio of about 51 : 49 and 55 : 45 for **1** and **2**, respectively.

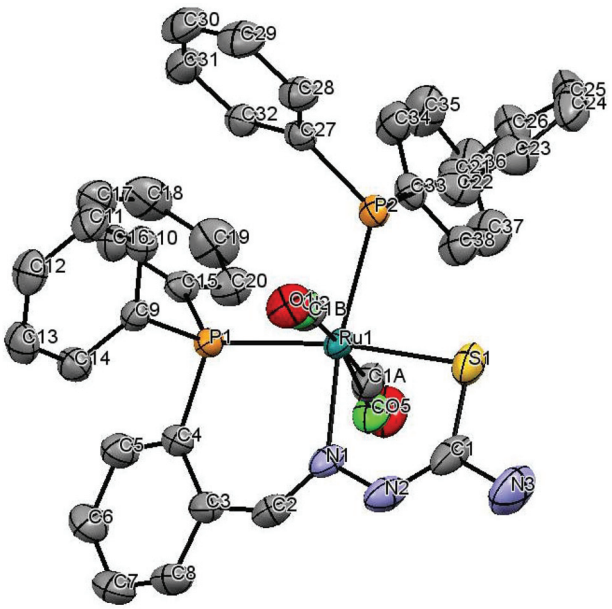


Fig. 1 ORTEP plot of complex [RuCl(CO)(PPh_3)(PNS-H)] (**1**). Thermal ellipsoids have been drawn at the 50% probability level. Hydrogen atoms and the solvent are omitted for clarity. Carbonyl and chloride ligands are located in two positions, owing to disorder.

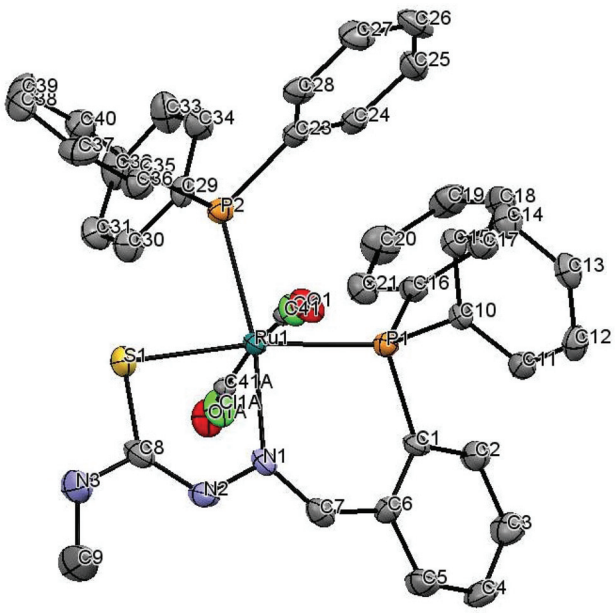


Fig. 2 ORTEP plot of [RuCl(CO)(PPh_3)(PNS-Me)] (**2**). Thermal ellipsoids have been drawn at the 50% probability level and hydrogen atoms are omitted for clarity. Carbonyl and chloride ligands are located in two positions, owing to disorder.

90.63(7) [N(1)–Ru(1)–P(1)] and 81.21(7) [N(1)–Ru(1)–S(1)]. This results in significant distortion of the {$RuP_2NS(CO)Cl$} core from the ideal octahedral geometry, which is reflected in the twelve *cis* and three *trans* angles. As expected, the PPh_3 ligand occupies mutually *cis* position to the PPh_2 head in the thiosemicarbazone chain for better π interaction.[35b] The large deviation of the [P(1)–Ru(1)–P(2)] angle [99.78(3)] from 90 may be ascribed to the steric repulsion between the two adjacent

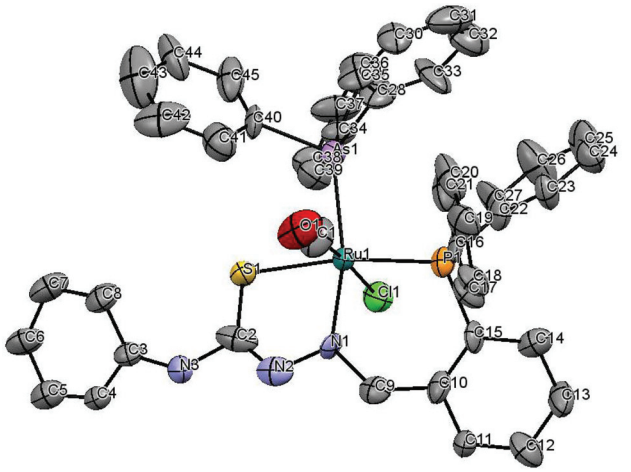


Fig. 3 ORTEP plot of complex [RuCl(CO)($AsPh_3$)(PNS-Ph)] (**6**). Thermal ellipsoids have been drawn at the 50% probability level and hydrogen atoms are omitted for clarity.

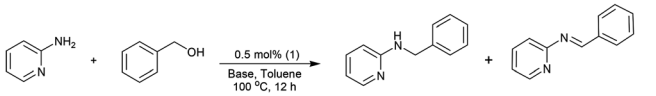
bulky phosphine molecules. The equatorial bond lengths are 2.127(11) [Ru(1)–N(1)] Å, 2.125(3) Å [Ru(1)–P(2)], 2.3859(8) [Ru(1)–S(1)] Å and Ru(1)–P(2) = 2.3982(8) Å. For complexes bearing P, N-iminophosphine ligands, the higher *trans* influence of the phosphorus atom in comparison to that of the imine donor functionality leads to longer distances for bonds *trans* to the phosphorus.[36] On the other hand, in the presence of tridentate P,N,S ligands (with N being an iminic nitrogen) the reverse situation is usually observed;[15] the related bond distances in [RuCl(CO)(PPh_3)(PNS-H)] (namely, Ru(1)–N(1) = 2.125(3) Å, Ru(1)–P(2) = 2.3982(8)) follow this rule. The other two axial sites are occupied by a carbonyl group and one chlorine ligand with Ru(1)–C(1A) and Ru(1)–Cl(1) distances of 1.88(2) Å and 2.441(4) Å. The CO group occupies the site *trans* to the Cl (N(1)–Ru1–P(2) = 169.37(7)). This may be a consequence of strong $Ru^{II}\rightarrow CO$ back donation as indicated by the short Ru–C [1.88(2) Å] bond and the low CO stretching frequency (1949 cm^{-1}), which prefers σ or π weak donor groups occupying the site opposite to CO to favor the d–π back donation.

After a careful search of the literature concerning ruthenium complexes derived from thiosemicarbazone ligands, we have found several examples of ruthenium complexes with the XNS (O, N, C) thiosemicarbazone ligand type.[8b,16,37] Nevertheless, complexes containing Ru PNS thiosemicarbazone are still scarce. Taking this fact into account, we must stress the novelty of the ruthenium(II) complexes (**1–6**) reported in this article, because it is the first example of phosphine-functionalized thiosemicarbazone ruthenium(II) complexes.

Catalytic studies

Optimization for N-alkylation reaction conditions. To investigate a promising catalytic system, a screen was performed for a model reaction between 2-aminopyridine and benzyl alcohol. Representative results are shown in Table 3. In the absence of a base, N-alkylation of amine was not observed (entry 1). Weak

Table 3 Optimization of N-alkylation reaction conditions[a]



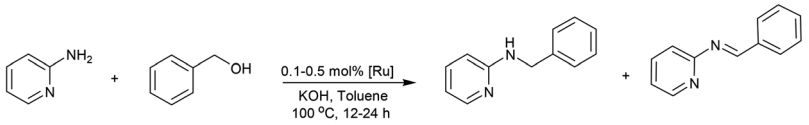
Entry	Base	Alcohol–amine–base	Yield[b] (%)	Amine[c] (%)
1	—	1 : 1	0	—
2	K_2CO_3	1 : 1 : 1	0	—
3	K_2CO_3	1 : 1 : 2	0	—
4	K_2CO_3	1 : 1 : 3	0	—
5	KOH	1 : 1 : 1	90	86
6	KOH	1 : 1 : 1.5	92	90
7	**KOH**	**1 : 1 : 2**	**94**	**94**
8	KOH	1 : 1 : 3	94	94
9	KO*t*-Bu	1 : 1 : 1	88	62
10	KO*t*-Bu	1 : 1 : 1.5	93	67
11	KO*t*-Bu	1 : 1 : 2	96	74
12	KO*t*-Bu	1 : 1 : 3	95	75
13	NaOH	1 : 1 : 2	95	78
14	$NaHCO_3$	1 : 1 : 2	0	—

[a] Reaction conditions: 2.00 mmol of benzyl alcohol, 2.00 mmol of 2-aminopyridine, base (4 mmol), catalyst **1** (0.5 mol%) in 5 mL of toluene at 100 °C. [b] Based on GC-MS of a crude reaction mixture. [c] Conversions determined by GC-MS. Formation of the corresponding imine as a byproduct accounts for the difference in conversion.

bases such as K_2CO_3 and $NaHCO_3$ were ineffective (entries 1–2 and 14). The reaction was considerably accelerated by the addition of a strong base (entries 5–13). When the reaction was carried out in the presence of KOH, *N*-benzylaminopyridine was formed in an excellent yield (up to 99%), which we considered to be the choice for the base (entries 5–8). Other strong bases such as KO*t*Bu and NaOH were also found effective (entries 9–12 and 13). In addition, to obtain almost quantitative yields and avoid the presence of the imine as a secondary product, from a lack of hydrogenation of the condensation product, at least 2 equivalents of the base with respect to the substrate are needed.

The ability to use small amounts of a catalyst and still achieve high conversions is of great importance in N-alkylation reactions due to the high cost of the metals and ligands used. We continued the N-alkylation reaction optimization process after finding the need for a strong base to activate the ruthenium complex **1**. The following step was to study the influence of the terminal substituents, coligands and catalyst loadings on the catalytic activity. The results are summarized in Table 4. The blank experiment was carried out without a catalyst, and no product formation is observed under these conditions, which excluded the contribution of base itself as a catalyst (entry 1). The results indicate that lower catalyst loadings lead to moderate yields, and longer reaction times are required to achieve maximum conversion (entries 2–13). Also, as expected, higher catalyst loadings led to higher yields and higher amine content in the product distribution (entries 14–19). Furthermore, considering the results when 0.5 mol% of the catalyst was used, it is clear that ruthenium complexes containing the methyl group (entry 15) as a terminal substituent lead to higher yields than those containing hydrogen or

Table 4 Influence of terminal substituents, coligands and catalyst loading on the catalytic activity of ruthenium(II) complexes[a]



Entry	[Ru]	Terminal substituents (R)/coligands	Amount [Ru] (mol%)	Time (h)	Yield[b] (%)	Amine[c] (%)
1	—	—	—	24	—	—
2	**1**	H/PPh_3	0.1	24	71	52
3	**2**	Me/PPh_3	0.1	24	64	61
4	**3**	Ph/PPh_3	0.1	24	59	59
5	**4**	H/$AsPh_3$	0.1	24	68	45
6	**5**	Me/$AsPh_3$	0.1	24	67	59
7	**6**	Ph/$AsPh_3$	0.1	24	56	54
8	**1**	H/PPh_3	0.3	18	89	62
9	**2**	Me/PPh_3	0.3	18	84	82
10	**3**	Ph/PPh_3	0.3	18	75	76
11	**4**	H/$AsPh_3$	0.3	18	87	59
12	**5**	Me/$AsPh_3$	0.3	18	83	78
13	**6**	Ph/$AsPh_3$	0.3	18	74	74
14	**1**	H/PPh_3	0.5	12	83	82
15	**2**	**Me/PPh_3**	**0.5**	**12**	**>99**	**>99**
16	**3**	Ph/PPh_3	0.5	12	92	91
17	**4**	H/$AsPh_3$	0.5	12	81	78
18	**5**	Me/$AsPh_3$	0.5	12	97	97
19	**6**	Ph/$AsPh_3$	0.5	12	90	89

[a] N-alkylation reaction conditions: 2.00 mmol of benzyl alcohol, 2.00 mmol of 2-amino pyridine, KOH (4 mmol), catalyst (0.1–0.5 mol%) in 5 mL of toluene at 100 °C. [b] Based on GC-MS of a crude reaction mixture. [c] Conversions determined by GC-MS. Formation of the corresponding imine as a byproduct accounts for the difference in conversion.

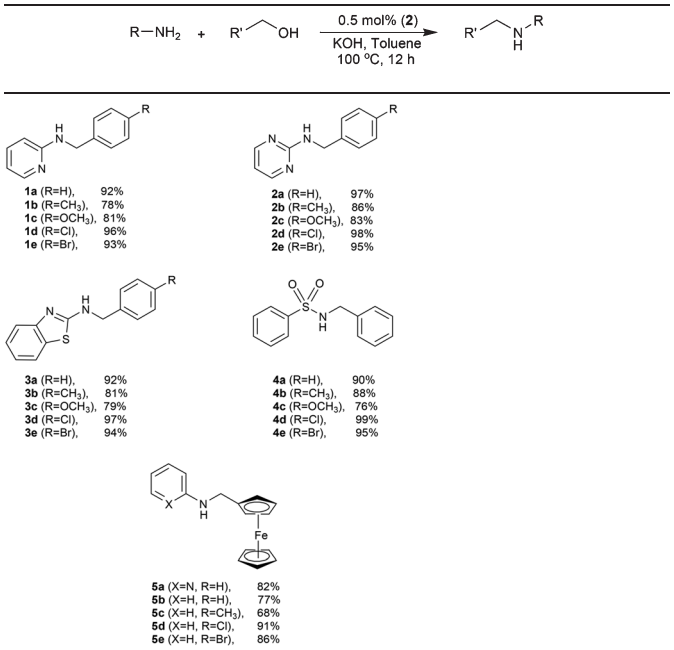
phenyl (entries 14 and 16) and significantly shorter reaction times are needed to complete the N-alkylation process. This behavior indicates that steric effects may also play an important role in terms of catalyst efficiency or in terms of the generation of the catalytically active species. In addition, complexes **1**, **3**, and **6** showed good activity at lower catalyst loadings, but when the catalyst concentration was increased, it was not possible to obtain yields as high as those with their analogues. However, it is important to note that, among complexes with methyl substituents in the terminal positions, those containing PPh_3 and $AsPh_3$ coligands (**2** and **5**) showed the best selectivity toward the synthesis of the amine (entries 15 and 18). Thus, electronic properties may also account for the catalytic activity, although not as much as steric effects.

We believe that the catalytic amine alkylation with ruthenium(II) complexes follows the 'borrowed hydrogen' pathway, extensively studied by Williams, Fujita, Yamaguchi and others.[19–27] The alcohol is catalytically dehydrogenated to the corresponding aldehyde (*in situ* oxidation) in the first step. Then, the aldehyde condenses with the amine to give an intermediate imine, which is subsequently hydrogenated (reduction) by the catalyst. Thus, there is no net H_2 consumption in this process; however, the reaction benefits from being run in a closed system preventing irreversible H_2 loss.

N-alkylation of heterocyclic amines and amides. In order to check the versatility of our catalysts, we decided to study the substrate scope of catalyst **2** with other amine/amide and alcohol derivatives. The results shown in Table 5 summarize the effect of the substrates on the yield and selectivity of the catalytic reaction, using a 0.5 mol% loading of the catalyst in toluene at 100 °C. The reactions of 2-aminopyridine with benzyl alcohols bearing electron-donating and -withdrawing substituents at the aromatic ring proceeded smoothly to give the corresponding *N*-benzylaminopyridine in good to high yields (**1a–1e**). Benzyl alcohols with *p*-MeO, *p*-Cl and *p*-Br were tolerant (**1c–1e**). The reaction of sterically demanding 2-methylbenzyl alcohol also proceeded to give the corresponding amine in good yield (**1b**). Similar to the case of 2-aminopyridine, the N-alkylation of 2-aminopyrimidine with benzyl alcohol and *para*-methyl, -methoxy substituted benzyl alcohols gave the corresponding products **2a–2c** with 97, 86 and 83% yields, respectively. The N-alkylation with benzyl alcohols bearing a halogen atom (Cl or Br) proceeded to give the corresponding products **2d** and **2e** with excellent yields as well. 2-Aminobenzothiazole also reacted with benzylic alcohols to afford the desired products in 92, 81, 79, 97 and 94% yields, respectively (**3a–3e**). Interestingly, the reaction of *p*-toluenesulfonamide with benzylic alcohols afforded the corresponding alkylated sulfonamide in good to excellent yields (76–99%; **4a–4e**). The present protocol also performed for N-alkylation of amines such as aminobenzene, 2-aminopyridine, 4-methyl, 4-chloro and 4-bromoaniline with ferrocenemethanol in high yield (**5a–5e**).

It is worth mentioning that complex **2** can also catalyze the direct amination of 2-nitropyridine with benzyl alcohol, which is more sustainable for the synthesis of amines.[38] Typically, a mixture of 2-nitropyridine, potassium hydroxide, catalyst **2** and

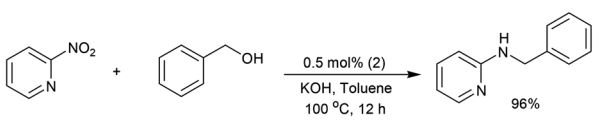
Table 5 N-alkylation of (hetero)aromatic amine/amide with alcohols catalyzed by **2**[a,b]



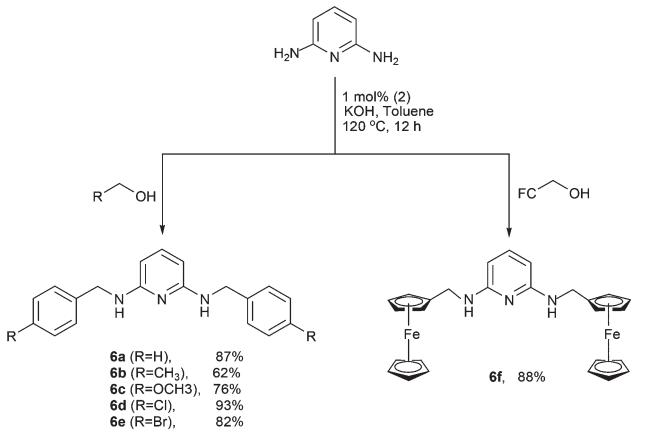
[a] Reaction conditions: 2.00 mmol of alcohol, 2.00 mmol of amine/amide, base (4 mmol), catalyst **2** (0.5 mol%) in 5 mL of toluene at 100 °C. [b] Isolated yields.

benzyl alcohol was heated at 100 °C for 12 h, and *N*-benzylpyridine was obtained in 96% yield (Scheme 4). Apparently, the reduction of a nitro group can be achieved by a hydrogen transfer reduction with **2**.

N-alkylation of heteroaromatic diamine. One of the outstanding properties of the present catalyst is its high selectivity for monoalkylation of heteroaromatic amines. Hence, it was of interest to determine whether this selectivity for the monoalkylation of primary aromatic functions could be used for the N,N-dialkylation of diamines. Only very few synthetic procedures for the preparation of such compounds can be found in the literature.[39] In most cases, these transformations are either not selective or have to be performed in several steps and thus lack in general applicability towards a broad range of substrates.[40] As evident from the results in Scheme 5, it is possible to selectively monoalkylate both amino functions of the diamine, affording the corresponding product (**6a–6f**) in excellent yields. First, 2,6-diaminopyridine was reacted with benzyl alcohol, which afforded *N*,*N*′-dibenzylpyridine-2,6-diamine (87%; **6a**). Next, several substituted benzyl alcohols were employed and, as determined before for the alkylation of heterocyclic amines (Table 5), both electron-donating and electron-withdrawing substituents in the *para* position are well-tolerated, these reactions affording the dialkylated products in yields ranging from 62 to 93% (**4a–4e**). Also, the reaction with ferrocenemethanol did not distress the yield of the corresponding dialkylated product (**6f**).



Scheme 4 Direct amination of nitropyridine with benzyl alcohol.

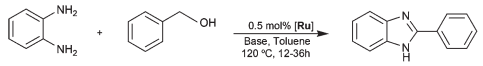


Scheme 5 Selective N,N′-dialkylation of diamine with alcohols catalyzed by **2**, and the isolated yields in %. Reaction conditions: 4 mmol of alcohol, 2.00 mmol of diamine, base (4 mmol), catalyst **2** (1 mol%) in 5 mL of toluene at 120 °C.

N-alkylation of *ortho*-substituted anilines: synthesis of benzimidazoles, benzothiazoles and benzoxazoles. The most commonly used methods for the synthesis of benzazoles include the condensation of *ortho*-substituted (–NH_2 or –SH or –OH) anilines with aldehydes,[41] nitriles,[42] carboxylic acids,[43] or acyl chlorides.[44] Most of these methods are associated with limitations such as poor selectivity, side reactions, tedious work-up procedures and requirement of a special oxidation process. Alternatively, few reports are also available on the synthesis of benzazoles directly from alcohols.[45] Recently, Ru/Xanthphos,[46] Ru,[47] and IBX[48] have been applied for the synthesis of benzimidazoles. Deng *et al.* reported dppf [1,1′-bis(diphenylphosphino)ferrocene] catalyzed synthesis of 2-arylbenzoxazoles directly from *o*-nitrophenols and benzyl alcohols.[49]

Although the reaction conditions were similar to those of the N-alkylation, the reaction took a longer time for completion at slightly higher temperatures. Various experiments were carried out to optimize the N-alkylation of *ortho*-substituted anilines (Table 6). In order to explore the scope of the present method, the reactions of *o*-substituted (–NH_2 or –OH or –SH) anilines were successfully performed with a variety of alcohols (Table 7). The reaction of *o*-phenylenediamine was carried out with benzyl alcohol to obtain 2-phenylbenzimidazole (**7a**) in 93% yield. Functionalized alcohols, such as 4-methoxybenzyl alcohol and 4-chlorobenzyl alcohol, were utilized to afford the corresponding products **7b** and **7c** in 81 and 98% yields, respectively. Heterocyclic alcohol, 2-pyridylmethanol, gave the corresponding product (**7d**) in high yield. However, a low yield was obtained with an aliphatic alcohol, isoamyl alcohol (**7e**). The reaction of 2-aminophenol with benzyl alcohol and benzyl alcohols bearing an electron-donating group and an electron-withdrawing group afforded the

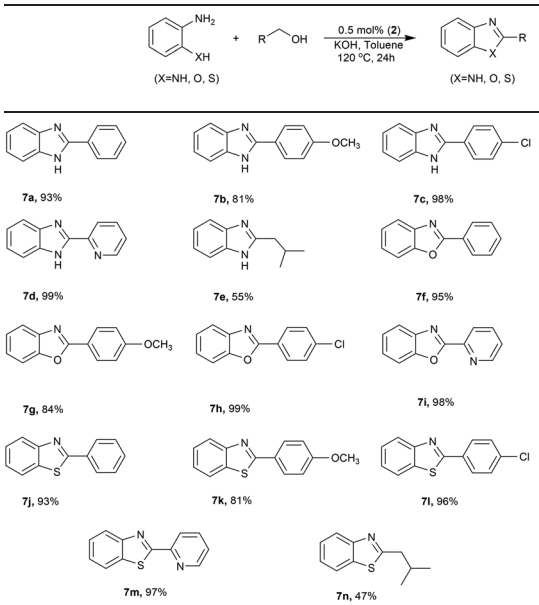
Table 6 Optimization of reaction conditions for the synthesis of 2-aryl-benzazoles catalyzed by ruthenium(II) complexes[a]



Entry	[Ru]	Terminal substituents (R)/coligands	Base	Time (h)	Yield[b] (%)
1	—	—	KOH	24	5
2	**1**	H/PPh_3	KOH	12	78
3	**1**	H/PPh_3	KOH	24	81
4	**2**	CH_3/PPh_3	KOH	12	90
5	**2**	**CH_3/PPh_3**	**KOH**	**24**	**93**
6	**2**	CH_3/PPh_3	KOH	36	93
7	**3**	C_6H_5/PPh_3	KOH	24	88
8	**4**	H/$AsPh_3$	KOH	24	75
9	**5**	CH_3/$AsPh_3$	KOH	24	90
10	**6**	C_6H_5/$AsPh_3$	KOH	24	82
11	**2**	CH_3/PPh_3	KO*t*-Bu	24	53
12	**2**	CH_3/PPh_3	NaOH	24	66
13	**2**	CH_3/PPh_3	K_2CO_3	24	7
13	**2**	CH_3/PPh_3	$NaHCO_3$	24	11
14	—	—	KOH	24	82[c]

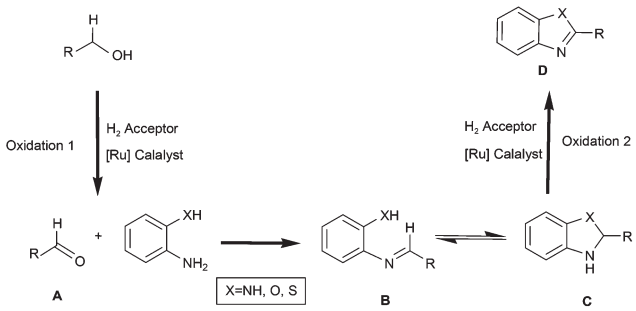
[a] Reaction conditions: 3.00 mmol of benzyl alcohol, 2.00 mmol of, *o*-phenylenediamine, base (4 mmol), catalyst (0.5 mol%) in 5 mL of toluene at 120 °C. [b] GC-MS yield. Reaction with benzaldehyde (2 mmol). [c] Reaction with benzaldehyde (2 mmol).

Table 7 N-alkylation of *o*-heterosubstituted aniline with alcohols catalyzed by **2**[a,b]



[a] Reaction conditions: 3 mmol of alcohol, 2.00 mmol of *o*-heterosubstituted aniline, base (4 mmol), catalyst **2** (0.5 mol %) in 5 mL of toluene at 120 °C. [b] Isolated yields.

corresponding products **7f–7i** with 84–99% yields respectively. In addition, heteroaromatic alcohol gave the corresponding benzothioazole product in high yield. Reaction of aminothiophenol with benzyl alcohol and 4-substituted benzyl alcohols afforded the desired 2-aryl substituted benzoxazoles in excellent yields. In the case of benzyl alcohol (93%, **7k**), 4-methoxybenzyl alcohol (81%, **7l**) and 4-chlorobenzyl alcohol (96%, **7m**), good to excellent yields were observed. The reaction was also applied to 2-pyridylmethanol, but the desired products were obtained in low yield.



Scheme 6 Plausible mechanism of ruthenium catalyzed N-alkylation of *o*-heterosubstituted anilines.

A possible mechanism to rationalize this transformation is illustrated in Scheme 6. Starting from alcohol, catalytic hydrogen transfer to an appropriate H_2 acceptor (Ru catalyst) *via* "Oxidation 1" would lead to the formation of aldehyde **A**. Condensation of **A** with *ortho*-substituted anilines generate an intermediate imine **B**, which can be in equilibrium with dihydrobenzazole **C**. A second hydrogen-transfer process from **C** then provides a route to benzazole **D** *via* "Oxidation 2" with the ruthenium(II) catalyst. To confirm this, controlled experiments were carried out with and without the ruthenium catalyst (entries 1 and 5 respectively, Table 6). The yield of the desired product decreased drastically without the ruthenium catalyst. On the other hand reaction of *o*-phenylenediamine with benzaldehyde instead of alcohol in the absence of a catalyst gave 85% of 2-phenylbenzimidazole (entry 14, Table 6). This confirmed that the ruthenium catalyst is mainly involved in the oxidation of alcohols to aldehydes. Further experiments are ongoing to explain these results.

Conclusions

We have reported the synthesis and characterization of novel air-stable complexes [RuCl(CO)(EPh_3)(L)] (**1–6**), in which the substituents on the terminal position of the ligands and coligands have been modified. The crystal structures of three of the complexes prepared, **1**, **2**, and **6**, have been described. The catalytic study of [RuCl(CO)(EPh_3)(L)] complexes **1–6** toward amine N-alkylation and one-pot synthesis of benzoxazoles was completed, showing that all catalysts are active toward catalytic transformations. The results also showed that steric effects in the ligands play a more important role than electronic effects in the catalytic activity of the new complexes. In the N-alkylation process, complex **2** has been proven to be a versatile and efficient catalyst under mild conditions in comparison to its analogues and other ruthenium and iridium complexes.[50] Also, complex **2** has shown high tolerance to functional groups

in the amine and alcohol moieties. The present process is applicable for the direct amination of 2-nitropyridine with benzyl alcohol leading to the secondary amine with **2** as the catalyst. Furthermore, complex **2** has been proven to selectively catalyze the synthesis of N,N-dialkylated amine when diamines are used as substrates. On the other hand, complex **2** has been proven to be a very efficient and versatile catalyst for the synthesis of 2-substituted benzimidazoles, benzoxazoles and benzothiazoles.

Experimental section

General

Unless otherwise noted, all reactions were performed under an atmosphere of air. Thin-layer chromatography (TLC) was performed on Merck 1.05554 aluminum sheets precoated with silica gel 60 F254, and the spots were visualized with UV light at 254 nm or under iodine. Column chromatography purifications were performed by using Merck silica gel 60 (0.063–0.200 mm). Elemental analyses (C, H, N, S) were performed on a Vario EL III Elemental analyzer. Infrared spectra of the ligands and the metal complexes were recorded as KBr discs in the range of 4000–400 cm^{-1} using a Nicolet Avatar model FT-IR spectrophotometer. The electronic spectra of the complexes were recorded with a Shimadzu UV-1650 PC spectrophotometer using dichloromethane as the solvent. ^{1}H (300 and 400 MHz), ^{13}C (100 MHz) and ^{31}P NMR (162 MHz) spectra were taken in DMSO or $CDCl_3$ at room temperature with a Bruker AV400 instrument with chemical shifts relative to tetramethylsilane (^{1}H, ^{13}C) and *o*-phosphoric acid (^{31}P). Mass spectra were recorded on a LC-MS Q-ToF Micro Analyzer (Shimadzu), using the electrospray ionization (ESI) mode. GC-mass spectrometry was performed using a JEOL GCMATE II GC-MS system. The melting points were recorded with a Lab India melting point apparatus.

Commercially available $RuCl_3{\cdot}3H_2O$ was used as supplied from Loba Chemie Pvt. Ltd. All the reagents used in this study were of Analar grade, and the solvents were purified and dried according to standard procedures. Triphenylphosphine/triphenylarsine, 2-(diphenylphosphino)-benzaldehyde and thiosemicarbazone derivatives were purchased from Aldrich and were used as received. The ruthenium metallic precursors $[RuHCl(CO)(PPh_3)_3]$ and $[RuHCl(CO)(AsPh_3)_3]$ were prepared according to literature methods.[51]

Synthesis of the ligands

The ligands 2-(2-(diphenylphosphino)benzylidene) thiosemicarbazone (**PNS-H**) and 2-(2-(diphenylphosphino)benzylidene)-*N*-methylthiosemicarbazone (**PNS-Me**) 2-(2-(diphenylphosphino)benzylidene)-*N*-phenylthiosemicarbazone (**PNS-Ph**) were prepared following the procedure reported previously.[9–15]

Synthesis of the complexes

$[RuCl(CO)(PPh_3)(PNS\text{-}H)]$ (1). A suspension of $[RuHCl(CO)(PPh_3)_3]$ (0.100 g, 0.105 mmol) in ethanol (15 mL) was treated with **PNS-H** (0.038 g, 0.105 mmol) and the mixture was gently refluxed for 6 h. During this time, the color changed to orange. After it was cooled to room temperature, the suspension was filtered and the orange solid was thoroughly washed with cold ethanol and diethyl ether. Yield 78% (0.10 g), mp: 256–258 °C. Anal. Calcd for $C_{39}H_{32}ClN_3OP_2RuS$: C, 59.35; H, 4.09; N, 5.32; S, 4.06. Found: C, 59.49; H, 4.12; N, 5.14; S, 4.26. IR (KBr disks, cm^{-1}): 3434 (ms, ν_{NH}); 3064 (m, ν_{NH}); 1949 (s, $\nu_{C\equiv O}$); 1582 + 1474 (s, $\nu_{C=N}$ + ν_{C-N}); 742 (s, ν_{C-S}); 1434, 1089, 693 (s, for PPh_3). UV-Vis (CH_2Cl_2), λ_{max} (nm): 234, 258, 343, 427. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 8.73 (d, 1H, J = 8.8 Hz, CH═N), 8.50 (s, –NH_2), 7.71–7.53 (m, 4H, Ar H), 7.49–7.19 (m, 14H, Ar H), 7.13–7.09 (m, 4H, Ar H), 6.67 (t, 7H, J = 8.0 Hz, Ar H), 6.55–6.51 (m, 4H, Ar H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) = 206.73 (C≡O), 176.12 (C–S), 154.60 (–CH═N), 138.82 (Ar C), 137.43 (Ar C), 137.24 (Ar C), 136.05 (Ar C), 135.70 (Ar C), 135.60 (Ar C), 133.50 (Ar C), 133.36 (Ar C), 132.94 (Ar C), 129.87 (Ar C), 129.12 (Ar C), 129.01 (Ar C), 128.85 (Ar C), 128.78 (Ar C), 128.01 (Ar C), 127.44 (Ar C), 125.55 (Ar C), 125.26 (Ar C). ^{31}P NMR (162 MHz, DMSO-d_6): δ (ppm) = 30.05 (d, J = 22.6 Hz, PPh_3), 28.74 (d, J = 22.6 Hz, PPh_2). MS (ESI, m/z): 753.6 $[M - Cl]^+$. Single crystals suitable for an X-ray determination were grown by slow evaporation of dichloromethane–methanol solution of **1** at room temperature.

$[RuCl(CO)(PPh_3)(PNS\text{-}Me)]$ (2). It was prepared as described for **1** by the suspension of $[RuHCl(CO)(PPh_3)_3]$ (0.100 g, 0.105 mmol) with **PNS-Me** (0.039 g, 0.105 mmol). Yield 73% (0.10 g), mp: 254–256 °C. Anal. Calcd for $C_{40}H_{34}ClN_3OP_2RuS$: C, 59.81; H, 4.27; N, 5.23; S, 3.99. Found: C, 59.49; H, 4.09; N, 5.14; S, 4.26. IR (KBr disks, cm^{-1}): 3420 (ms, ν_{NH}); 1945 (s, $\nu_{C\equiv O}$); 1584 + 1471 (s, $\nu_{C=N}$ + ν_{C-N}); 747 (s, ν_{C-S}); 1432, 1091, 695 (s, PPh_3). UV-Vis (CH_2Cl_2), λ_{max} (nm): 233, 245, 355, 430. ^{1}H NMR (400 MHz, DMSO): δ (ppm) = 8.75 (d, 1H, J = 8.0 Hz –CH═N); 8.57 (s, 1H, –NH), 7.62–7.58 (m, 1H, Ar H), 7.56–7.13 (m, 24H, Ar H), 6.89 (t, 2H, J = 10.8 Hz, Ar H), 6.78 (t, 1H, J = 11.2 Hz, Ar H), 6.72 (t, 2H, J = 11.6 Hz, Ar H), 1.22 (s, 3H, –CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) = 206.48 (C≡O), 176.45 (C–S), 155.53 (–CH═N), 136.48 (Ar C), 135.27 (Ar C), 133.84 (Ar C), 132.17 (Ar C), 131.95 (Ar C), 130.71 (Ar C), 130.61 (Ar C), 130.55 (Ar C), 130.38 (Ar C), 130.27, (Ar C), 129.65 (Ar C), 127.91 (Ar C), 127.86 (Ar C), 127.79 (Ar C), 127.65 (Ar C), 127.53 (Ar C), 127.30 (Ar C), 126.51 (Ar C), 126.33 (Ar C), 125.45 (Ar C), 123.81 (Ar C), 123.53 (Ar C), 31.17 (–CH_3). ^{31}P NMR (162 MHz, DMSO-d_6): δ (ppm) = 30.15 (d, J = 22.6 Hz, PPh_3), 28.85 (d, J = 25.9 Hz, PPh_2). MS (ESI, m/z): 794.1 $[M - Cl]^+$. Orange colored crystals obtained in the reaction mixture itself were found to be suitable for X-ray diffraction.

$[RuCl(CO)(PPh_3)(PNS\text{-}Ph)]$ (3). It was prepared as described for **1** by the suspension of $[RuHCl(CO)(PPh_3)_3]$ (0.100 g, 0.105 mmol) with **PNS-Ph** (0.039 g, 0.105 mmol). Yield 78% (0.10 g), mp: 254–256 °C. Anal. Calcd for $C_{45}H_{36}ClN_3OP_2RuS$: C, 62.46; H, 4.19; N, 4.86; S, 3.71. Found: C, 62.61; H, 4.21; N, 4.94; S, 3.91. IR (KBr disks, cm^{-1}): 3390 (ms, ν_{NH}); 1962 (s, $\nu_{C\equiv O}$); 1591 + 1482 (s, $\nu_{C=N}$ + ν_{C-N}); 738 (s, ν_{C-S}); 1433, 1092, 694 (s, PPh_3). UV-Vis (CH_2Cl_2), λ_{max} (nm): 236, 256, 369, 428.

^{1}H NMR (400 MHz, DMSO-d$_6$): δ (ppm) = 8.75 (d, 1H, J = 8.7 Hz, –CH═N), 8.60 (s, 1H, –NH), 7.68 (d, 2H, J = 8.4 Hz, Ar H), 7.63 (s, 2H, Ar H), 7.57–7.46 (m, 9H, Ar H), 7.33 (t, 6H, J = 6.3 Hz, Ar H), 7.25–7.16 (m, 9H, Ar H), 7.06 (t, 2H, J = 7.2 Hz, Ar H), 6.90 (t, 1H, J = 6.9 Hz, Ar H), 6.78 (t, 1H, J = 8.4 Hz, Ar H), 6.59 (t, 2H, J = 8.7 Hz, Ar H). ^{13}C NMR (100 MHz, DMSO-d$_6$): δ (ppm) = 206.40 (C≡O), 170.42 (C–S), 156.56 (–CH═N), 136.93 (Ar C), 136.76 (Ar C), 136.13 (Ar C), 136.05 (Ar C), 134.39 (Ar C), 133.81 (Ar C), 133.73 (Ar C), 133.50 (Ar C), 133.40 (Ar C), 133.30 (Ar C), 133.27 (Ar C), 133.08 (Ar C), 132.00 (Ar C), 131.90 (Ar C), 131.68 (Ar C), 131.30 (Ar C), 131.15 (Ar C), 130.58 (Ar C), 130.24 (Ar C), 129.96 (Ar C), 128.90 (Ar C), 128.91 (Ar C), 128.73 (Ar C), 128.66 (Ar C), 128.57 (Ar C), 128.48 (Ar C), 128.30 (Ar C), 128.05 (Ar C), 127.95 (Ar C), 127.75 (Ar C), 127.66 (Ar C), 126.66 (Ar C), 126.24 (Ar C), 121.16 (Ar C), 119.07 (Ar C). ^{31}P NMR (162 MHz, DMSO-d$_6$): δ (ppm) = 29.79 (d, J = 22.6 Hz, PPh_3), 28.85 (d, J = 22.6 Hz, PPh_2). MS (ESI, m/z): 830.2 $[M - Cl]^+$.

[RuCl(CO)(AsPh$_3$)(PNS-H)] (4). A suspension of [RuHCl(CO)-($AsPh_3$)$_3$] (0.100 g, 0.105 mmol) in ethanol (15 mL) was treated with **PNS-H** (0.038 g, 0.105 mmol) and the mixture was gently refluxed for 8 h. During this time, the colour changed to yellow. Then the solvent was removed under reduced pressure, and the solid was washed thoroughly with cold ethanol and diethyl ether, affording a shiny yellow crystalline solid. Yield 82% (0.11 g), mp: 110–112 °C. Anal. Calcd for $C_{39}H_{32}AsClN_3OPRuS$: C, 56.22; H, 3.87; N, 5.04; S, 3.85. Found: C, 56.49; H, 3.79; N, 5.14; S, 3.66. IR (KBr disks, cm^{-1}): 3392 (ms, ν_{NH}); 1962 (s, $\nu_{C\equiv O}$); 1592 + 1496 (s, $\nu_{C=N}$ + ν_{C-N}); 738 (s, ν_{C-S}); 1433, 1092, 694 (s, for $AsPh_3$). UV-Vis (CH_2Cl_2), λ_{max} (nm): 231, 245, 350, 427. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ (ppm) = 8.86 (d, 1H, J = 8.3 Hz, –CH═N), 8.48 (s, 1H, –NH$_2$), 7.86 (t, 1H, J = 7.2 Hz, Ar H), 7.75–7.02 (m, 23H, Ar H), 6.89 (t, 3H, J = 7.2 Hz, Ar H), 6.70 (t, 1H, J = 8.8 Hz, Ar H), 6.57 (m, 2H, J = 7.2 Hz, Ar H). ^{13}C NMR (100 MHz, DMSO-d$_6$): δ (ppm) = 206.02 (C≡O), 176.04 (C–S), 154.59 (–CH═N), 138.91 (Ar C), 136.53 (Ar C), 134.41 (Ar C), 134.02 (Ar C), 133.92 (Ar C), 133.52 (Ar C), 133.19 (Ar C), 133.11 (Ar C), 132.08 (Ar C), 131.81 (Ar C), 131.16 (Ar C), 130.64 (Ar C), 130.39 (Ar C), 130.02 (Ar C), 128.84 (Ar C), 128.66 (Ar C), 128.51 (Ar C), 128.17 (Ar C), 128.08 (Ar C), 125.21 (Ar C). ^{31}P NMR (162 MHz, DMSO-d$_6$): δ (ppm) = 32.13 (s, PPh_2). MS (ESI, m/z): 767.6 $[M - Cl]^+$.

[RuCl(CO)(AsPh$_3$)(PNS-Me)] (5). It was prepared as described for **4** by suspension of [RuHCl(CO)(APh_3)$_3$] (0.100 g, 0.092 mmol) with **PNS-Me** (0.034 g, 0.092 mmol). Yield 78% (0.10 g), mp: 120–122 °C. Anal. Calcd for $C_{40}H_{34}AsClN_3OPRuS$: C, 56.71; H, 4.05; N, 4.96; S, 3.78. Found: C, 56.87; H, 4.31; N, 4.81; S, 3.26. IR (KBr disks, cm^{-1}): 3423 (ms, ν_{NH}); 1945 (s, $\nu_{C\equiv O}$); 1585 + 1490 (s, $\nu_{C=N}$ + ν_{C-N}); 747 (s, ν_{C-S}); 1432, 1091, 695 (s, for $AsPh_3$). UV-Vis (CH_2Cl_2), λ_{max} (nm): 235, 257, 356, 435. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ (ppm) = 8.77 (d, 1H, J = 8.0 Hz, –CH═N), 8.15 (s, 1H, –NH), 7.63–7.10 (m, 24H, Ar H), 6.89–6.86 (m, 1H, Ar H), 6.72 (t, 1H, J = 7.6 Hz, Ar H), 6.55 (t, 2H, J = 8.0 Hz, Ar H), 1.22 (s, 3H, –CH$_3$). ^{13}C NMR (100 MHz, DMSO-d$_6$): δ (ppm) = 206.42 (C≡O), 176.03 (C–S), 154.27 (–CH═N), 138.91 (Ar C), 134.00 (Ar C), 133.90 (Ar C), 133.79 (Ar C), 133.54 (Ar C), 133.12 (Ar C), 132.91 (Ar C), 132.80 (Ar C), 131.79 (Ar C), 131.68 (Ar C), 131.38 (Ar C), 131.29 (Ar C), 131.03 (Ar C), 130.48 (Ar C), 130.32 (Ar C), 129.89 (Ar C), 129.06 (Ar C), 128.64 (Ar C), 128.41 (Ar C), 128.10 (Ar C), 128.00 (Ar C), 30.60 (–CH$_3$). ^{31}P NMR (162 MHz, DMSO-d$_6$): δ (ppm) = 32.73 (s, PPh_2). MS (ESI, m/z): 811.8 $[M - Cl]^+$.

[RuCl(CO)(AsPh$_3$)(PNS-Ph)] (6). It was prepared as described for **4** by suspension of [RuHCl(CO)($AsPh_3$)$_3$] (0.100 g, 0.092 mmol) with **PNS-Ph** (0.039 g, 0.092 mmol). Yield 76% (0.105 g), mp: 132–134 °C. Anal. Calcd for $C_{45}H_{36}AsClN_3OPRuS$: C, 59.44; H, 3.99; N, 4.62; S, 3.53. Found: C, 59.28; H, 3.89; N, 4.81; S, 3.26. IR (KBr disks, cm^{-1}): 3390 (ms, ν_{NH}); 1962 (s, $\nu_{C\equiv O}$); 1591 + 1482 (s, $\nu_{C=N}$ + ν_{C-N}); 738 (s, ν_{C-S}); 1433, 1092, 694 (s, for $AsPh_3$). UV-Vis (CH_2Cl_2), λ_{max} (nm): 235, 258, 367, 429. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ (ppm) = 8.74 (d, 1H, J = 7.6 Hz, –CH═N), 8.52 (s, 1H, –NH), 7.88–7.85 (m, 1H, Ar H), 7.74 (d, 2H, J = 7.6 Hz, Ar H), 7.63–7.10 (m, 27H, Ar H), 6.89 (t, 1H, J = 7.2 Hz, Ar H), 6.72–6.60 (m, 1H, Ar H), 6.57 (t, 2H, J = 8.8 Hz, Ar H). ^{13}C NMR (100 MHz, DMSO-d$_6$): δ (ppm) = 206.45 (C≡O), 170.73 (C–S), 155.68 (–CH═N), 135.48 (Ar C), 135.27 (Ar C), 133.84 (Ar C), 132.35 (Ar C), 131.17 (Ar C), 129.95 (Ar C), 124.40 (Ar C), 123.71 (Ar C), 123.61 (Ar C), 123.55 (Ar C), 123.38 (Ar C), 123.27 (Ar C), 122.65 (Ar C), 122.51 (Ar C), 122.36 (Ar C), 122.11 (Ar C), 121.89 (Ar C), 121.53 (Ar C), 121.20 (Ar C), 121.11 (Ar C), 120.73 (Ar C), 120.45 (Ar C), 119.02 (Ar C), 116.81 (Ar C), 115.82 (Ar C). ^{31}P NMR (162 MHz, DMSO-d$_6$): δ (ppm) = 31.38 (s, PPh_2). MS (ESI, m/z): 873.0 $[M - Cl]^+$. Single crystals suitable for an X-ray determination were grown by slow evaporation of dichloromethane–ethanol solution of **6** at room temperature.

Catalysis

Catalytic N-alkylation of (hetero)aromatic amines and amide with alcohols. A typical procedure is as follows. To a stirred suspension of ruthenium(II) catalyst (0.5 mol%) and KOH (4 mmol) in toluene (5 mL) were added alcohol (2.0 mmol) and amine/amide (2.0 mmol) at room temperature and then the temperature was raised to 100 °C for 12 h. Upon completion (as monitored by TLC), the reaction mixture was cooled at ambient temperature, H_2O (3 mL) was added and the organic layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried with magnesium sulfate and concentrated. The crude product was analyzed by GC-MS or purified by column chromatography (*n*-hexane–EtOAc). The reported isolated yields are the average of two runs.

Direct amination of 2-nitropyridine with benzyl alcohol. To a stirred suspension of ruthenium(II) catalyst (0.5 mol%) and KOH (4 mmol) in toluene (5 mL) were added benzyl alcohol (12.0 mmol) and 2-nitropyridine (2.0 mmol) at room temperature and then the temperature was raised to 100 °C for 12 h. Upon completion (as monitored by TLC), the reaction mixture was cooled at ambient temperature, H_2O (3 mL) was added and the organic layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried with magnesium sulphate and concentrated. The crude product was analyzed by GC-MS or

purified by column chromatography (*n*-hexane–EtOAc). The reported isolated yields are the average of two runs.

Catalytic N-alkylation of heteroaromatic diamine with alcohols. To a stirred suspension of ruthenium(II) catalyst (0.1 mol%) and KOH (4 mmol) in toluene (5 mL) were added alcohol (4 mmol) and diamine (2.0 mmol) at room temperature and then the temperature was raised to 120 °C for 12 h. Upon completion (as monitored by TLC), the reaction mixture was cooled at ambient temperature, H_2O (3 mL) was added and the organic layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were concentrated *in vacuo* and the crude product was analyzed by GC-MS or purified by column chromatography over silica-gel (*n*-hexane–ethyl acetate). The reported isolated yields are the average of two runs.

Typical procedure for the one-pot synthesis of 2-substituted benzazoles. To a stirred suspension of the ruthenium catalyst (0.5 mol%) and KOH (4 mmol) in toluene (5 mL) were added alcohol (3 mmol) and *o*-substituted aniline (2.0 mmol) at room temperature and then the temperature was raised to 120 °C for 24 h. Upon completion (as monitored by TLC), the reaction mixture was cooled at ambient temperature, H_2O (3 mL) was added and the organic layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were concentrated *in vacuo* and the crude product was analyzed by GC-MS or purified by column chromatography (*n*-hexane–EtOAc). The reported isolated yields are the average of two runs.

The catalytic reactions given in Tables 3–7 were similarly conducted. The resulting amines, amides, 2-aryl substituted benzimidazoles, benzoxazoles and benzothiazoles were identified by comparison of the ^1H and ^{13}C NMR data with those previously reported (S33–S60, ESI†).

X-ray crystallography

Crystals of **1**, **2** and **6** were mounted on glass fibers and used for data collection. Crystal data were collected at 295.0(2) K (**1**, **6**) using a Gemini A Ultra Oxford Diffraction automatic diffractometer or at 293.0(2) K (**2**) using a Stoe Mark II-Image Plate Diffraction system. Graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) was used throughout. The absorption corrections were performed by the multi-scan method. Corrections were made for Lorentz and polarization effects. The structures were solved by direct methods using the program SHELXS-97.[52] Refinement and all further calculations were carried out using SHELXL-97.[52] The H atoms were included in calculated positions and treated as riding atoms using the SHELXL default parameters. The non-hydrogen atoms were refined anisotropically using weighted full-matrix least squares on F^2. Atomic scattering factors were incorporated into the computer programs. In the solid state (**1** and **2**), a disorder is observed within the two different enantiomeric forms in such a manner that only the CO group and the chlorine atom share the ligand positions mutually. Despite several attempts to get better crystals of complex **6** and a better data set, only poor-quality data were obtained.

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References

1 (*a*) D. Aguila, E. Escribano, S. Speed, D. Talancon, L. Yerman and S. Alvarez, *Dalton Trans.*, 2009, 6610–6625; (*b*) A. L. Gavrilova and B. Bosnich, *Chem. Rev.*, 2004, **104**, 349–383.

2 For selected reviews, see: (*a*) T. S. Lobana, R. Sharma, G. Bawa and S. Khanna, *Coord. Chem. Rev.*, 2009, **253**, 977–1055; (*b*) T. S. Lobana, G. Bawa, A. Castineiras, R. J. Butcher and M. Zeller, *Organometallics*, 2008, **27**, 175–180; (*c*) T. S. Lobana, G. Bawa and R. J. Butcher, *Inorg. Chem.*, 2008, **47**, 1488–1495; (*d*) R. Archaryya, F. Basuli, S. M. Peng, G. H. Lee, L. R. Falvello and S. Bhattacharya, *Inorg. Chem.*, 2006, **45**, 1252–1259; (*e*) I. Pal, F. Basuli, T. C. W. Mak and S. Bhattacharya, *Angew. Chem., Int. Ed.*, 2001, **113**, 3007–3011; (*f*) J. S. Casas, M. S. G. Tasende and J. Sordo, *Coord. Chem. Rev.*, 2000, **209**, 197–261; (*g*) S. Padhi and G. B. Kauffman, *Coord. Chem. Rev.*, 1985, **63**, 127–160; (*h*) M. J. M. Campbell, *Coord. Chem. Rev.*, 1975, **15**, 297–319.

3 For selected examples, see: (*a*) P. K. Suganthy, R. N. Prabhu and V. S. Sreedevi, *Tetrahedron Lett.*, 2013, **54**, 5695–5698; (*b*) P. R. Verma, S. Mandal, P. Gupta and B. Mukhopadhyay, *Tetrahedron Lett.*, 2013, **54**, 4914–4917; (*c*) R. N. Prabhu and R. Ramesh, *Tetrahedron Lett.*, 2012, **53**, 5961–5965; (*d*) S. Datta, D. K. Seth, S. Gangopadhyay, P. Karmakar and S. Bhattacharya, *Inorg. Chim. Acta*, 2012, **392**, 118–130; (*e*) P. Paul, S. Datta, S. Halder, R. Acharyya, F. Basuli, R. J. Butcher, S.-M. Peng, G.-H. Lee, A. Castineiras, M. G. B. Drew and S. Bhattacharya, *J. Mol. Catal. A: Chem.*, 2011, **344**, 62–73; (*f*) T. S. Lobana, G. Bawa, R. J. Butcher, B. J. Liaw and C. W. Liu, *Polyhedron*, 2006, **25**, 2897–2903.

4 For selected examples, see: (*a*) D. Palanimuthu, S. V. Shinde, K. Somasundaran and A. G. Samuelson, *J. Med. Chem.*, 2013, **56**, 722–734; (*b*) J. L. Hickey and P. S. Donnelly, *Coord. Chem. Rev.*, 2012, **256**, 2367–2380; (*c*) P. V. Bernhardt, P. C. Sharpe, M. Islam, D. B. Lovejoy, D. S. Kalinowski and D. R. Richardson, *J. Med. Chem.*, 2009, **52**, 407–415; (*d*) A. G. Quiroga and C. N. Ranninger, *Coord. Chem. Rev.*, 2004, **248**, 119–133.

5 P. Pelagatti, A. Venturini, A. Leporati, M. Carcelli, M. Costa, A. Bacchi, G. Pelizzi and C. Pelizzi, *J. Chem. Soc., Dalton Trans.*, 1998, 2715–2721.

6 I. D. Kostas, G. A. Heropoulos, D. Kovala-Demertzi, P. N. Yadav, J. P. Jasinski, M. A. Demertzis,

F. J. Andreadaki, G. Vo-Thanh, A. Petit and A. Loupy, *Tetrahedron Lett.*, 2006, **47**, 4403–4407.

7 (*a*) R. N. Prabhu and R. Ramesh, *Tetrahedron Lett.*, 2013, **54**, 1120–1124; (*b*) G. Xie, P. Chellan, J. Mao, K. Chibale and G. S. Smith, *Adv. Synth. Catal.*, 2010, **352**, 1641–1647.

8 (*a*) M. Nirmala, R. Manikandan, G. Prakash and P. Viswanathamurthi, *Appl. Organomet. Chem.*, 2014, **28**, 18–26; (*b*) D. Pandiarajan and R. Ramesh, *Inorg. Chem. Commun.*, 2011, **14**, 686–689.

9 V. M. Leovac, B. Ribar, G. Argay, A. Kalman and I. Brceski, *J. Coord. Chem.*, 1996, **39**, 11.

10 G. Argay, A. Kalman, L. Parkanyi, V. M. Leovac, I. D. Brceski and P. N. Radivojsa, *J. Coord. Chem.*, 2000, **51**, 9–19.

11 U. Abram, K. Ortner, R. Gust and K. Sommer, *J. Chem. Soc., Dalton Trans.*, 2000, 735–744.

12 A. Castineiras, R. Pedrido and G. Perez-Alonso, *Eur. J. Inorg. Chem.*, 2008, 5106–5111.

13 A. Castineiras and R. Pedrido, *Inorg. Chem.*, 2008, **47**, 5534–5536.

14 A. Castineiras and R. Pedrido, *Inorg. Chem.*, 2009, **48**, 4847–4855.

15 A. Castineiras and R. Pedrido, *Dalton Trans.*, 2010, **39**, 3572–3584.

16 (*a*) P. Kalaivani, R. Prabhakaran, P. Poornima, F. Dallemer, K. Vijayalakshmi, V. Vijaya Padma and K. Natarajan, *Organometallics*, 2012, **31**, 8323–8332; (*b*) R. Prabhakaran, P. Kalaivani, R. Huang, M. Sieger, W. Kaim, P. Viswanathamurthi, F. Dallemer and K. Natarajan, *Inorg. Chim. Acta*, 2011, **376**, 317–324.

17 (*a*) S. A. Lawerencem, *Amines: Synthesis Properties and Applications*, Cambridge University, Cambridge, 2004; (*b*) A. Seayad, M. Ahmed, H. Klein, R. Jackstell, T. Gross and M. Beller, *Science*, 2002, **297**, 1676–1678; (*c*) K. P. C. Vollhardt and N. E. Schore, *Organic Chemistry: Structure and Function*, ed. W. H. Freeman, New York, 3rd edn, 1999, p. 936.

18 (*a*) J. F. Hartwig, *Synlett*, 2006, 1283–1294; (*b*) S. L. Buchwald, C. Mauger, G. Mignani and U. Scholz, *Adv. Synth. Catal.*, 2006, **348**, 23–39; (*c*) R. N. Salvatore, C. H. Yoon and K. W. Jung, *Tetrahedron*, 2001, **57**, 7785–7811; (*d*) J. S. Bradshaw, K. E. Krakowiak and R. M. Izatt, *Tetrahedron*, 1992, **48**, 4475–4515.

19 For selected reviews, see: (*a*) T. Suzuki, *Chem. Rev.*, 2011, **111**, 1825–1845; (*b*) R. H. Crabtree, *Organometallics*, 2011, **30**, 17–19; (*c*) G. E. Dobereiner and R. H. Crabtree, *Chem. Rev.*, 2010, **110**, 681–703; (*d*) G. Guillena, D. J. Ramon and M. Yus, *Chem. Rev.*, 2010, **110**, 1611–1641; (*e*) T. D. Nixon, M. K. Whittlesey and J. M. J. Williams, *Dalton Trans.*, 2009, 753–765.

20 For selected examples, see: (*a*) F. Li, H. Shan, L. Chen, Q. Kang and P. Zou, *Chem. Commun.*, 2012, **48**, 603–605; (*b*) O. Saidi, A. J. Blacker, M. M. Farah, S. P. Marsden and J. M. J. Williams, *Chem. Commun.*, 2010, **46**, 1541–1543; (*c*) R. Kawahara, K. Fujita and R. Yamaguchi, *J. Am. Chem. Soc.*, 2010, **132**, 15108–15111; (*d*) Y.-H. Chang, C.-F. Fu, Y.-H. Liu, S.-M. Peng, J.-T. Chen and S.-T. Liu, *Dalton Trans.*, 2009, 861–867; (*e*) A. P. Da Costa, M. Sanau, E. Peris and B. Royo, *Dalton Trans.*, 2009, 6960–6966; (*f*) O. Saidi, A. J. Blacker, M. M. Farah, S. P. Marsden and J. M. J. Williams, *Angew. Chem., Int. Ed.*, 2009, **48**, 7375–7378.

21 For selected examples, see: (*a*) S. Bahn, S. Imm, L. Neubert, M. Zhang, H. Neumann and M. Beller, *Chem.–Eur. J.*, 2011, **17**, 4705–4708; (*b*) M. Zhang, S. Imm, S. Bahn, H. Neumann and M. Beller, *Angew. Chem., Int. Ed.*, 2011, **50**, 11197–11201; (*c*) A. Tillack, D. Hollmann, K. Mevius, D. Michalik, S. Bahn and M. Beller, *Eur. J. Org. Chem.*, 2008, 4745–4750; (*d*) D. Hollmann, A. Tillack, D. Michalik, R. Jackstell and M. Beller, *Chem.–Asian J.*, 2007, **2**, 403–410.

22 (*a*) A. J. A. Watson and J. M. J. Williams, *Science*, 2010, **329**, 635–636; (*b*) M. H. S. A. Hamid, C. L. Allen, G. W. Lamb, A. C. Maxwell, H. C. Maytum, A. J. A. Watson and J. M. J. Williams, *J. Am. Chem. Soc.*, 2009, **131**, 1766–1774; (*c*) M. H. S. A. Hamid and J. M. J. Williams, *Chem. Commun.*, 2007, 725–727.

23 (*a*) A. J. A. Watson, A. C. Maxwell and J. M. J. Williams, *J. Org. Chem.*, 2011, **76**, 2328–2331; (*b*) D. Pingen, C. Muller and D. Vogt, *Angew. Chem., Int. Ed.*, 2010, **49**, 8130–8133; (*c*) C. Gunanathan and D. Milstein, *Angew. Chem., Int. Ed.*, 2008, **120**, 8789–8792.

24 For selected examples, see: (*a*) S. Agrawal, M. Lenormand and B. M. Matute, *Org. Lett.*, 2012, **14**, 1456–1459; (*b*) B. Blank, M. Madalska and R. Kempe, *Adv. Synth. Catal.*, 2008, **350**, 749–758; (*c*) M. H. S. A. Hamid and J. M. J. Williams, *Chem. Commun.*, 2007, 725–727; (*d*) S. Naskar and M. Bhattacharjee, *Tetrahedron Lett.*, 2007, **48**, 3367–3370; (*e*) A. Del Zotto, W. Baratta, M. Sandri, G. Verardo and P. Rigo, *Eur. J. Inorg. Chem.*, 2004, 524–529; (*f*) Y. Watanabe, Y. Morisaki, T. Kondo and T. Mitsudo, *J. Org. Chem.*, 1996, **61**, 4214–4218.

25 (*a*) P. Pigeon, S. Top, A. Vessieres, M. Huche, M. Gormen, M. E. Arbi, M. A. Plamont, M. J. McGlinchey and G. Jaouen, *New J. Chem.*, 2011, **35**, 2212–2218; (*b*) C. Biot, B. Pradines and D. Dive, in *Ferroquine: A Concealed Weapon*, ed. K. Becker, Wiley-VCH, 2011, 397–411; (*c*) D. C. Cole, W. J. Lennox, S. Lombardi, J. W. Ellingboe, R. C. Bernotas, G. J. Tawa, H. Mazandarani, D. L. Smith, G. Zhang, J. Coupet and L. E. Schechter, *J. Med. Chem.*, 2005, **48**, 353–356; (*d*) M. Banerjee, A. Poddar, G. Mitra, A. Surolia, T. Owa and B. Bhattacharyya, *J. Med. Chem.*, 2005, **48**, 547–555; (*e*) J. Drew, *Science*, 2000, **287**, 1960–1964.

26 (*a*) N. J. Liverton, R. A. Bednar, B. Bednar, J. W. Butcher, C. F. Claiborne, D. A. Claremon, M. Cunningham, A. G. DiLella, S. L. Gaul, B. E. Libby, E. A. Lyle, J. J. Lynch, J. A. McCauley, S. D. Mosser, K. T. Nguyen, G. L. Stump, H. Sun, H. Wang, J. Yergey and K. S. Koblan, *J. Med. Chem.*, 2007, **50**, 807–819; (*b*) C. Biot, G. Glorian, L. A. Maciejewski, J. S. Brocard, O. Domarle, G. Blampain, P. Millet, A. J. Georges, H. Abessolo, D. Dive and J. Lebibi, *J. Med. Chem.*, 1997, **40**, 3715–3718.

27 (*a*) C. Liu, J. Lin, S. Pitt, R. F. Zhang, J. S. Sack, S. E. Kiefer, K. Kish, A. M. Doweyko, H. Zhang, P. H. Marathe, J. Trzaskos, M. Mckinnon, J. H. Dodd, J. C. Barrish, G. L. Schieven and K. Leftheris, *Bioorg. Med. Chem. Lett.*,

2008, **18**, 1874–1879; (*b*) J. Van Heusden, R. Van Ginckel, H. Bruwiere, P. Moelans, B. Janssen, W. Floren, B. J. Van der Leede, J. Van Dun, G. Sanz, M. Venet, L. Dillen, C. Van Hove, G. Willemsens, M. Janicot and W. Wouters, *Br. J. Cancer.*, 2002, **86**, 605–611; (*c*) P. Jimonet, F. Audiau, M. Barreau, J. C. Blanchard, J. M. Stutzmann and S. Mignani, *J. Med. Chem.*, 1999, **42**, 2828–2843.

28 (*a*) A. A. Weekes and A. D. Westwell, *Curr. Med. Chem.*, 2009, **16**, 2430–2440; (*b*) D. A. Horton, G. T. Bourne and M. L. Smythe, *Chem. Rev.*, 2003, **103**, 893–930; (*c*) T. C. Kuhler, M. Swanson, V. Shcherbuchin, H. Larsson, B. Mellgard and J. E. Sjostrom, *J. Med. Chem.*, 1998, **41**, 1777–1788.

29 (*a*) F. Kallashi, D. Kim, J. Kowalchick, Y. J. Park, J. A. Hunt, A. Ali, C. J. Smith, M. L. Hammond, J. V. Pivnichny, X. Tong, S. S. Xu, M. S. Anderson, Y. Chen, S. S. Eveland, Q. Guo, S. A. Hyland, D. P. Milot, A. M. Curniskey, M. Latham, L. B. Peterson, R. Rosa, C. P. Sparrow, S. D. Wright and P. Sinclair, *J. Bioorg. Med. Chem. Lett.*, 2011, **21**, 558–561; (*b*) C. G. Mortimer, G. Wells, J. P. Crochard, E. L. Stone, T. D. Bradshaw, M. F. Stevens and A. D. Westwell, *J. Med. Chem.*, 2006, **49**, 179–185.

30 (*a*) R. Ramachandran and P. Viswanathamurthi, *Spectrochim. Acta, Part A*, 2013, **103**, 53–61; (*b*) P. Anitha, R. Manikandan, A. Endo, T. Hashimoto and P. Viswanathamurthi, *Spectrochim. Acta, Part A*, 2012, **99**, 174–180; (*c*) R. Manikandan, P. Viswanathamurthi and M. Muthukumar, *Spectrochim. Acta, Part A*, 2011, **83**, 297–303; (*d*) M. Muthukumar, S. Sivakumar, P. Viswanathamurthi, R. Karvembu and R. Prabhakaran, *J. Coord. Chem.*, 2010, **63**, 296–306; (*e*) M. Muthukumar and P. Viswanathamurthi, *Appl. Organomet. Chem.*, 2009, **23**, 78–85.

31 A. Castineiras and R. Pedrido, *Dalton Trans.*, 2012, **41**, 1363–1372.

32 R. Prabhakaran, S. Anantharaman, M. Thilagavathi, M. V. Kaveri, P. Kalaivani, R. Karvembu, N. Dharmaraj, H. Bertagnolli, F. Dallemer and K. Natarajan, *Spectrochim. Acta, Part A*, 2011, **78**, 844–853.

33 P. Tarasconi, S. Capacchi, G. Pelosi, M. Cornia, R. Albertini, A. Bonati, P. Dall'Aglio, P. Lunghi and S. Pinelli, *Bioorg. Med. Chem.*, 2000, **8**, 157–162.

34 P. Crochet, J. Gimeno, S. Garcıa-Granda and J. Borge, *Organometallics*, 2001, **20**, 4369–4377.

35 (*a*) D. Mavrynsky, J. Rahkila, D. Bandarra, S. Martins, M. Meireles, M. J. Calhorda, I. J. Kovacs, I. Zupko, M. M. Hanninen and R. Leino, *Organometallics*, 2013, **32**, 3012–3017; (*b*) R. Armstrong, C. Ecott, E. Mas-Marz, M. J. Page, M. F. Mahon and M. K. Whittlesey, *Organometallics*, 2010, **29**, 991–997; (*c*) F. Basuli, S. M. Peng and S. Bhattacharya, *Inorg. Chem.*, 2001, **40**, 1126–1133.

36 (*a*) T. F. Vaughan, D. J. Koedyk and J. L. Spencer, *Organometallics*, 2011, **30**, 5170–5180; (*b*) O. Del Campo, A. Carbayo, J. V. Cuevas, G. Garcia-Herbosa and A. Munoz, *Eur. J. Inorg. Chem.*, 2009, 2254–2260; (*c*) K. S. Coleman, M. L. H. Green, S. I. Pascu, N. H. Rees, A. R. Cowley and L. H. Rees, *J. Chem. Soc., Dalton Trans.*, 2001, 3384–3395.

37 M. Maji, M. Chatterjee, S. Ghosh, S. K. Chattopadhyay, B-M. Wu and T. C. W. Mak, *J. Chem. Soc., Dalton Trans.*, 1999, 135–140.

38 (*a*) C.-C. Lee and S.-T. Liu, *Chem. Commun.*, 2011, **47**, 6981–6983; (*b*) C. Feng, Y. Liu, S. Peng, Q. Shuai, G. Deng and C.-J. Li, *Org. Lett.*, 2010, **12**, 4888–4891.

39 (*a*) V. Sprinzak, *J. Am. Chem. Soc.*, 1956, **78**, 3207–3208; (*b*) J. Bernstein, B. Stearns, E. Shaw and W. A. Lott, *J. Am. Chem. Soc.*, 1947, **69**, 1151–1158.

40 (*a*) J. W. Sibert, G. R. Hundt, A. L. Sargent and V. Lynch, *Tetrahedron*, 2005, **61**, 12350–12357; (*b*) X. Liu, A. H. Eisenberg, C. L. Stern and C. A. Mirkin, *Inorg. Chem.*, 2001, **40**, 2940–2941; (*c*) R. Margalef-Catal, C. Claver, P. Salagre and E. Fernandez, *Tetrahedron Lett.*, 2000, **41**, 6583–6588.

41 (*a*) Y. Riadi, R. Mamouni, R. Azzalou, M. El Hadded, S. Routier, G. Guillaumet and S. Lazar, *Tetrahedron Lett.*, 2011, **52**, 3492–3495; (*b*) H. M. Bacchav, S. B. Bhagat and V. N. Telvekar, *Tetrahedron Lett.*, 2011, **52**, 5697–5701.

42 D. F. Shi, T. D. Bradshaw, S. Wrigley, C. J. McCall, P. Lelieveld, I. Fichtner and M. F. Stevens, *J. Med. Chem.*, 1996, **39**, 3375–3384.

43 (*a*) J. A. Seijas, T. Vazquez, M. Pilar, R. Carballido, M. Raquel, C. J. Crecente and L. Romar-Lopez, *Synlett*, 2007, 313–317; (*b*) J. Charton, S. Girault-Mizzi and C. Sergheraert, *Chem. Pharm. Bull.*, 2005, **53**, 492–497.

44 V. K. Tondon and M. Kumar, *Tetrahedron Lett.*, 2004, **45**, 4185–4187.

45 C. D. Wilfred and R. J. K. Taylor, *Synlett*, 2004, 1628–1630; V. R. Ruiz, A. Corma and M. I. Sabater, *Tetrahedron Lett.*, 2010, **66**, 730–735.

46 G. M. Raghavendra, A. B. Ramesha, C. N. Revanna, K. N. Nandeesh, K. Mantelingu and K. S. Rangappa, *Tetrahedron Lett.*, 2011, **52**, 5571–5574.

47 A. J. Blacker, M. M. Farah, M. I. Hall, S. P. Marsden, O. Saidi and J. M. J. Williams, *Org. Lett.*, 2009, **11**, 2039–2042.

48 J. N. Moorthy and I. Neogi, *Tetrahedron Lett.*, 2011, **52**, 3868–3871.

49 M. Wu, X. Hu, J. Liu, Y. Liao and G. J. Deng, *Org. Lett.*, 2012, **14**, 2722–2725.

50 (*a*) Y.-H. Chang, Y. Nakajima and F. Ozawa, *Organometallics*, 2013, **32**, 2210–2215; (*b*) F. E. Fernandez, M. Carmen Puerta and P. Valerga, *Organometallics*, 2012, **31**, 6868–6879; (*c*) C.-C. Lee, W.-Y. Chu, Y.-H. Liu, S.-M. Peng and S.-T. Liu, *Eur. J. Inorg. Chem.*, 2011, 4801–4806; (*d*) C. Xu, L. Y. Goh and S. A. Pullarkat, *Organometallics*, 2011, **30**, 6499–6502; (*e*) S. Kegnæs, J. Mielby, U. V. Mentzel, C. Christensen and A. Riisager, *Green Chem.*, 2010, **12**, 1437–1441.

51 (*a*) N. Ahmed, S. J. Levison, S. D. Robinson and M. F. Uttley, *Inorg. Synth.*, 1974, **15**, 48–52; (*b*) R. A. Sanchez-delgado, W. Y. Lee, S. R. Choi, Y. Cho and M. J. Jun, *Transition Met. Chem.*, 1991, **16**, 241–244.

52 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 2008, **64**, 112–122.

