N-Heterocyclic Carbenes, Part 25[+]

Polymer-Supported Carbene Complexes of Palladium: Well-Defined, Air-Stable, Recyclable Catalysts for the Heck Reaction

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Abstract: *N*-Heterocyclic dicarbene chelate complexes of formula [*cis*-$CH_2\{\overline{N(H)C{=}C(H)N(R)C}\}_2PdX_2$] (X = Br, I; R = $(CH_2)_nOH$; $n = 2$, 3) have been prepared and structurally characterized (for X = I, $n = 2$). The complexes were immobilized on a functionalized polystyrene support (Wang resin) through one of the oxygen centres. The complexes efficiently catalyze the Heck reaction of activated and non-activated arylbromides, are recyclable under aerobic conditions and exhibit hardly any leaching, which is in line with our theoretical investigations on ligand dissociation energies related to Pd^0 and Pd^{II} centres.

Keywords: C–C coupling · carbene complexes · catalysts · immobilization · palladium

Introduction

The recent advances regarding efficient catalysts for the Heck reaction have typified those made in the wider field of palladium-catalyzed C–C and C–heteroatom coupling reactions in the last five years, by the use of well-defined catalysts that are appropriate to the task instead of commercially available metal sources or those which do not benefit from any ligand activation.[1] This has resulted in systems which convert deactivated aryl bromides and, in some cases, activated aryl chlorides with decent turnover numbers. The reaction now shows promise for the industrial production of important chemicals, for example, styrene and cinnamic ester derivatives that are required as precursors for polymers, UV absorbers and antioxidants, and as intermediates in pharmaceuticals.[2] The field has been reviewed recently;[1, 3] specifically, major improvements have included, i) air and thermally stable Pd^{II} catalysts,[4] ii) Pd^0 complexes of highly basic, sterically hindered phosphines,[5] iii) water soluble catalyst systems[6] and iv) the use of molten salts as reaction media.[7] However, a practically useful heterogeneous catalyst is still to be developed.[2]

Herein, we report our studies of a heterogeneous, anchored molecular catalyst for the Heck reaction that exhibits excellent activities towards activated and non-activated bromoarene substrates. The catalyst system was chosen owing to i) the high activity of the molecular catalyst in the homogeneously catalyzed conversion of deactivated aryl halides,[8] ii) its stability under the reaction conditions commonly employed for the Heck reaction and iii) theoretical investigations that anticipated neglible palladium leaching from the support.

Results and Discussion

In earlier reports on the homogeneous catalysis of the Heck reaction, we have shown that both *P,C*-palladacyclic complexes, $[\{o\text{-}(\overline{CH_2})C_6H_4P(R)_2PdX\}_2]$,[4a, 7, 8c] and *N*-heterocyclic carbene (NHC) complexes, [*cis*-$CH_2\{\overline{N(H)C{=}C(H)N(R)C}\}_2PdX_2$],[8a,b] are efficient catalysts.

Theoretical investigations of the dissociation of NHC ligands from palladium centres: To further validate the choice of dicarbene complexes as being suitable for heterogeneous catalytic applications, we have studied a number of model reactions to access the binding strength of imidazolin-2-

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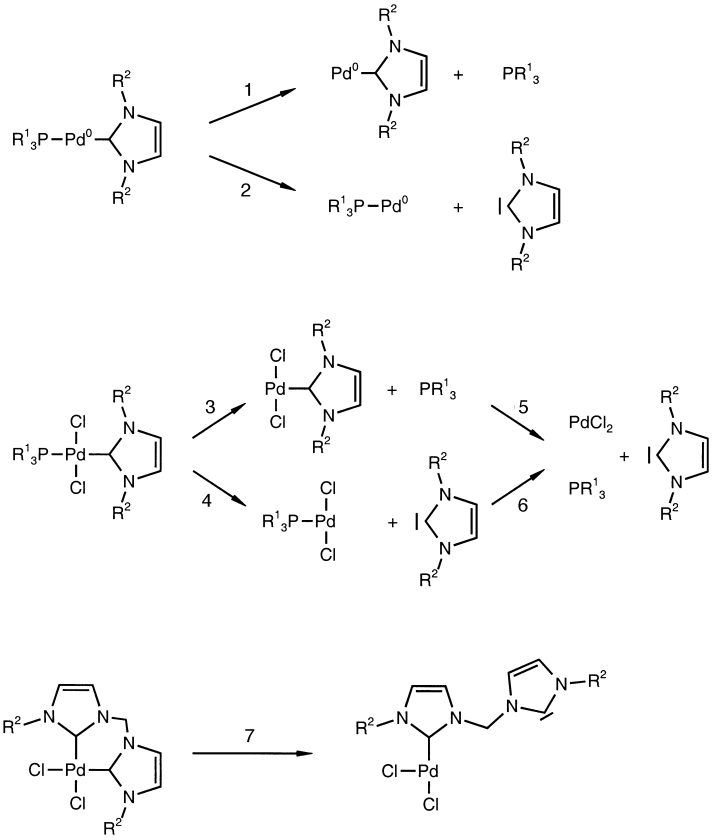
ylidene-based carbene ligands,[9] as compared with phosphine ligands, to palladium(0) and palladium(II) metal centres. A previous study on the bonding of the former ligands to coinage metal complexes suggested very high binding energies, which mainly originate from a largely electrostatic ligand-to-metal σ-donor interaction with only little π back-bonding.[10] In contrast, phosphines in general are considered to have non-negligible π-acceptor and σ-donor abilities, depending on the substituents.[11] We have calculated the Pd–P binding energies for both PH_3 and PMe_3, the latter being a stronger σ-donor than the former. It was shown in previous studies that PMe_3 dissociation energies compare much better with those for phosphine ligands commonly used in catalysis (i.e., PPh_3, PCy_3) than with PH_3 dissociation energies.[12, 27]

The model two-coordinate Pd^0 complex, $[Pd(PH_3)(NHC)]$, dissociates by loss of PH_3 or the free NHC, with relative dissociation energies of $+30.1$ and $+41.3$ kcal mol^{-1} (Table 1),

Table 1. Dissociation energies of reactions depicted in Scheme 1 calculated at BP86/DZVP.

Reaction	Substituents	ΔE [kcal mol^{-1}]
1	$R^1 = R^2 = H$	+ 30.1
2	$R^1 = R^2 = H$	+ 41.3
3	$R^1 = R^2 = H$	+ 27.6
	$R^1 = Me$; $R^2 = H$	+ 38.4
4	$R^1 = R^2 = H$	+ 61.0
	$R^1 = Me$; $R^2 = H$	+ 54.4
5	$R^2 = H$	+ 78.3
	$R^2 = Me$	+ 74.8
6	$R^1 = H$	+ 44.9
	$R^1 = Me$	+ 62.4
7	$R^2 = H$	+ 50.2



Scheme 1. Dissociation reactions 1–7 subject to theoretical calculations.

respectively (Reactions 1 and 2 in Scheme 1). In comparison, the analogous reactions at a palladium(II) centre were found to further disfavour the dissociation of the carbene ligand. The loss of PH_3 from $[PdCl_2(PR_3)(NHC)]$ requires $+27.6$ kcal mol^{-1} ($+38.4$ kcal mol^{-1} for PMe_3), relative to the loss of NHC, which requires $+61.0$ kcal mol^{-1} (Reactions 3 and 4 in Scheme 1). The stronger *trans* effect of PMe_3 as compared with PH_3 slightly decreases the dissociation energy of the carbene ligand to 54.4 kcal mol^{-1}. Further dissociation of the remaining ligand to yield $PdCl_2$ and the free ligand (Reactions 5 and 6 in Scheme 1) requires $+78.3$ kcal mol^{-1} for NHC and 44.9 kcal mol^{-1} for PH_3 (62.4 kcal mol^{-1} for PMe_3). However, the latter processes reflect ligand dissociation from a highly electron-deficient metal centre. Thus, dimer or oligomer formation can assist the dissociation process in solution, which we did not consider in this study. The opening of the six-membered palladacycle of [*cis*-$CH_2\{\overline{N(H)C{=}C(H)N(H)C}\}_2PdCl_2$] is energetically slightly more disfavoured than the dissociation of the corresponding monodentate carbene ligand and requires $+50.2$ kcal mol^{-1} (Reaction 7, Scheme 1).

The calculations show, in accord with earlier studies on other transition metals[12, 27] and in agreement with more qualitative considerations,[11] that PMe_3 is considerably more tightly bound to palladium(II) than PH_3. Still, the phosphine dissociation process is more likely to take place than NHC dissociation. Substitution of N–H by N–Me in the NHC introduces only minor changes in the dissociation energies as long as steric effects are negligible and electronic factors dominate. One can anticipate from these initial results that for NHC complexes, steric effects can be tuned independently of electronic effects by the choice of the *N*-bound substituents.

The calculations clearly demonstrate that imidazolin-2-ylidene-based carbene ligands bind to both Pd^0 and Pd^{II} centres substantially stronger than phosphine ligands, which have traditionally been successful in this type of catalytic processes.[1–4] In accord with previous studies,[10] the trends in dissociation energies identify the carbene ligands as strong σ donors, with very little π-acceptor character. The dissociation energies increase in the order $PH_3 < PMe_3 < NHC(H) \approx NHC(Me)$, correlating with the electron deficiencies at the palladium centres in the various complexes.

In summary, the results highlight the strong binding of the imidazolin-2-ylidene-carbene ligands to both Pd^0 and Pd^{II} dihalide systems relative to phosphine ligands; this lead us to believe that this system is highly suitable for attachment to solid supports owing to its anticipated low level of leaching.

Synthesis and characterization of molecular carbene complexes: The 1,1′-di(alkyl)-3,3′-methylenediimidazolium dihalide salts **1a** and **1b** were prepared from the appropriate alkyl

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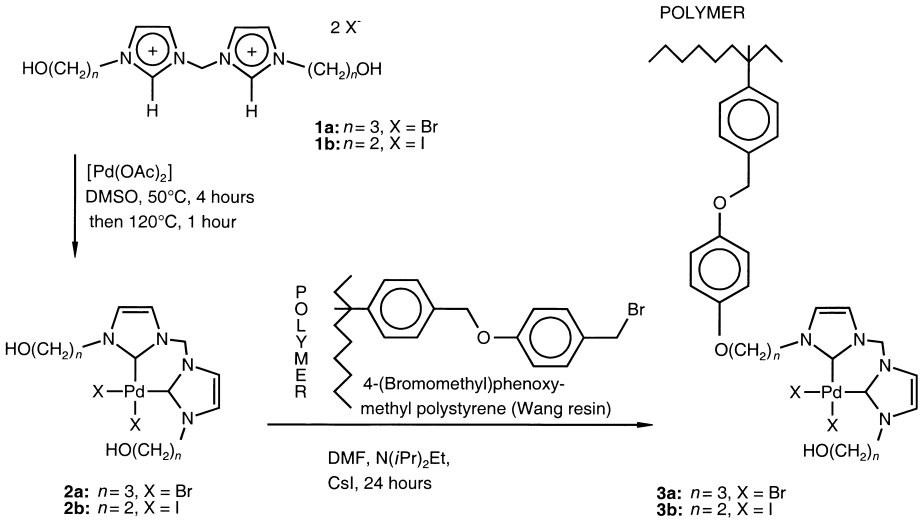
bromides and *N*,*N*′-diimidazolylmethane by adaptations of standard procedures.[13] The dicarbene palladium(II) dibromide complexes **2a** and **2b** were synthesized by our optimized procedure (Scheme 2).[14]

Crystals of complex **2b** suitable for X-ray structure determination were grown by vapor diffusion of ethanol into a concentrated dimethylsulfoxide solution. The crystal structure determination of complex **2b** showed the compound to be monomeric, with the dicarbene ligand chelating the palladium(II) centre in a *cis* fashion with the six-membered C_3N_2Pd ring in a boat conformation. The molecule possesses non-crystallographic C_s symmetry that passes through the palladium and methylene carbon centres (Figure 1). There is also a non-coordinating molecule of dimethylsulfoxide in the crystal lattice. The two −OH groups of the *N*-substituents do not interact with the distorted square-planar coordinated palladium centre; instead H bonding is observed with the oxygen atom of the non-coordinating dimethylsulfoxide molecule. This weak interaction results in short O···O distances (2.733(7) and 2.746(7) Å) and large O−H−O angles (175(10)° and 164(6)°). Summaries of important bond lengths and angles for complex **2b** appear in Table 2.



Scheme 2. Reaction scheme for the formation of **2a**, **2b**, **3a** and **3b**.

The Pd−C bond lengths of complex **2b**, 1.991(5) and 1.994(5) Å, compare with those found in the cationic[13a] and neutral chelating[8b] dicarbene palladium complexes $[cis\text{-}CH_2\{NC{=}CN(Me)C\}_2Pd(NCCH_3)_2]^{2+}[2\,PF_6]^-$ and $[cis\text{-}CH_2\{NC{=}CN(Me)C\}_2PdI_2]$ at 1.966(2) and 1.972(3) Å, and 1.988(7) and 1.989(8) Å, respectively. They also agree well with the calculated Pd−C bond length of 2.01 Å of the model chelate compound, $[cis\text{-}CH_2\{NC{=}CN(H)C\}_2PdCl_2]$, presented in the theoretical part of this study (see above). Angular distortions from the ideal square-planar geometry for the palladium centres in complex **2b** are minimal, with the exception of those introduced by the six-membered chelate ring for the bidentate dicarbene ligand.[13]

C−C and C−N bond lengths within the imidazolin-2-ylidene-based ring systems in complex **2b** are consistent with previous observations.[13, 14, 15] Other bond lengths and angles within the molecule of **2b** are unexceptional and do not require comment.

^1H and ^{13}C NMR spectra of complexes **2a** and **2b** are in agreement with their assigned

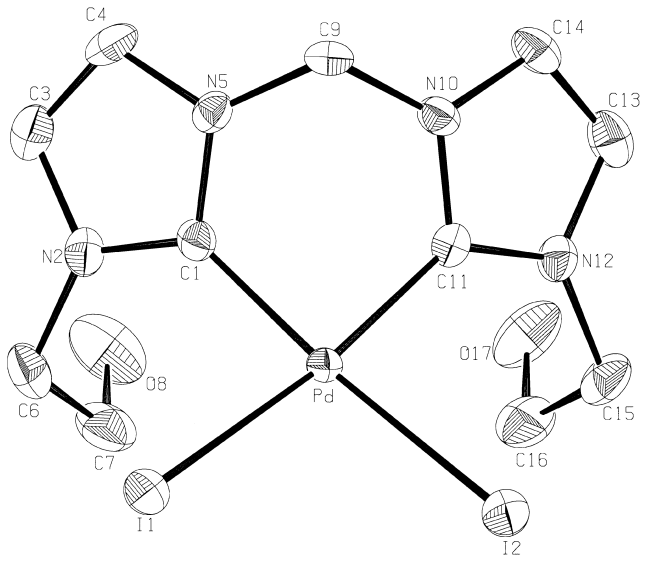


Figure 1. Molecular structure of compound **2b**.

Table 2. Selected bond lengths [Å] and angles [°] for compound **2b**.

I1−Pd	2.6755(5)	C6−C7	1.508(9)
I2−Pd	2.6546(5)	C13−C14	1.333(8)
Pd−C1	1.991(5)	C15−C16	1.506(9)
Pd−C11	1.994(5)	O8−C7	1.394(9)
O17−C16	1.393(9)	N2−C3	1.373(7)
N2−C1	1.355(6)	N2−C6	1.454(8)
N5−C9	1.448(6)	N5−C1	1.347(6)
N5−C4	1.374(7)	N10−C11	1.353(6)
N10−C14	1.379(7)	N10−C9	1.449(6)
N12−C11	1.350(6)	N12−C13	1.390(7)
N12−C15	1.471(7)	C3−C4	1.338(8)
I1-Pd-I2	89.73(2)	N2-C6-C7	112.5(5)
I1-Pd-C1	92.65(14)	O8-C7-C6	113.8(5)
I1-Pd-C11	169.75(15)	N5-C9-N10	109.2(4)
I2-Pd-C1	174.52(14)	N10-C11-N12	104.5(4)
I2-Pd-C11	93.24(13)	Pd-C11-N10	120.3(3)
C1-Pd-C11	83.59(19)	Pd-C11-N12	135.2(4)
N12-C13-C14	107.2(5)	N10-C14-C13	106.6(5)
N12-C15-C16	111.5(5)	O17-C16-C15	113.1(6)
C1-N2-C3	109.8(4)	C1-N2-C6	126.4(5)
C3-N2-C6	123.7(5)	C1-N5-C9	122.1(4)
C1-N5-C4	111.2(4)	C4-N5-C9	126.3(4)
C9-N10-C14	125.6(4)	C11-N10-C14	111.3(4)
C9-N10-C11	122.8(4)	C11-N12-C15	126.4(5)
C13-N12-C15	122.9(5)	C11-N12-C13	110.4(4)
N2-C1-N5	104.9(4)	Pd-C1-N5	121.1(3)
Pd-C1-N2	133.9(4)	N2-C3-C4	107.9(5)
N5-C4-C3	106.1(5)		

structures. The appearance of equivalent methylene proton resonances for complexes **2a** and **2b** indicates that inversion of the boat-shaped six-membered chelate rings is relatively fast on the ^{1}H NMR timescale. Such fluxional ring systems have been noted previously in related complexes, as have examples which were conformationally rigid at room temperature.[8b, 13, 14, 16] The IR spectra of complexes **2a** and **2b** show strong −OH absorption bands at 3446.0 cm^{-1} (**2a**) and 3422.2 cm^{-1} (**2b**). Other physical and spectroscopy features are unexceptional and will not be commented on further.

Synthesis, structural and spectroscopic characterization of polymer-supported catalysts: The *p*-bromomethylphenyl-functionalized polystyrene (Wang resin) was chosen, owing to the ready attachment of the accessible 1,1′-{*n*-HO(CH$_2$)$_n$} ($n = 2$, 3) disubstituted (dicarbene)palladium(II) dihalide complexes **2a** and **2b** to the support through an ether linkage by adaptations of existing procedures for the attachment of amines[17] and carboxylic acids (Scheme 2).[18]

Solid-state ^{13}C NMR spectra of the palladium-loaded polymers **3a** confirm the presence of the imidazolin-2-ylidene carbene ligand system; the characteristic resonances for both the carbene carbon and the methylene carbon of the NCH$_2$N bridge of the two imidazolin-2-ylidene ring systems ($\delta =$ 160.04 and 69.45, respectively) appearing close to those found in the molecular analogue **2a** ($\delta = 164.45$ and 67.48, respectively).

The IR spectra of the palladium loaded polymers **3a** and **3b** retain −OH absorption bands (3443.6 cm^{-1} and 3448.3 cm^{-1}, respectively), shifted only slightly from those found for complexes **2a** and **2b** (3446.0 cm^{-1} and 3422.2 cm^{-1}, respectively), but have intensities of the order of a 50% reduction relative to those observed for complexes **2a** and **2b**. This indicates the presence of residual alcohol functionalities of the polymer-attached palladium complex, which possibly exists as the mono-ether species depicted in Scheme 2. The palladium loading of the polymers **3a** and **3b** were consistently found to be in the range of 1.0–1.2%, which is substantially less than the calculated palladium loading for one molecule of complexes **2a** and **2b** being bound to the site of each *p*-bromomethylphenyl functional group of the polystyrene support (6.95%, **2a**; 6.67%, **2b**). This fact, coupled with the residual alcoholic functional groups found on the polymers **3a** and **3b**, indicates that many of the *p*-bromomethylphenyl functional groups are inaccessible for grafting the palladium complexes and that there is only a small amount of *p*-bromomethylphenyl functional groups available which can form ethereal linkages to both alcoholic functional groups of the same palladium complex.

Catalysis of the Heck reaction: The palladium-catalyzed arylation of olefins has found wide application in organic synthesis. In this reaction homogeneous catalytic systems have shown to be highly efficient. In order to make the Heck reaction more attractive for industry, several heterogeneous variants have previously been presented.[19] An efficient example uses Pd^0 grafted MCM-41 material,[20] which is synthesized by vapor deposition of a volatile palladium complex onto the inside walls of the porous framework, followed by reduction. Other examples use nanostructured palladium clusters stabilized by propylene carbonate[21] or hydrophilic palladium complexes anchored in supported aqueous phases (glass-bead technology).[22]

The *N*-heterocyclic dicarbene complexes **2a** and **2b** and their immobilized counterparts **3a** and **3b** are excellent catalysts for the arylation of olefins with aryl bromides. The catalytic activity of these materials was investigated in detail with activated, non- and deactivated aryl halides, and with styrene or *n*-butyl acrylate as the vinylic substrate (Tables 3 and 4).

Full conversions are obtained for the coupling of *p*-bromoacetophenone with styrene or *n*-butyl acrylate after 15 hours with as little as 0.02–0.15 mol% of heterogeneous catalysts **3a** and **3b** (entries 1, 2, 6, 14 and 15, Table 4). Reaction between bromobenzene and *n*-butyl acrylate gives turn over numbers of up to 4100 (entries 3, 4, 9–11, 16 and 17, Table 4), which is comparable with many of the commonly used homogeneous Heck catalysts. Even less reactive, deactivated bromobenzene derivatives bearing electron-donating ether groups can be converted with turn over numbers in the range of 10^3–10^4 (entries 13, 18, 19 and 21, Table 4). When styrene is employed as the vinylic substrate, conversions are generally lowered by about 10–15% and substantial amounts (5–10%) of the isomers **II** and **III** are obtained (Scheme 3). Heterogeneous catalysts **3a** and **3b** exhibit no significant difference in their catalytic activity and selectivity. Yields and product distributions are similar to those obtained with the analogous homogeneous catalysts **2a** and **2b** (Table 3), and the turnover frequencies (h^{-1}) are lowered by about one order of magnitude in the heterogeneous case. In line with previous studies on homogeneous Heck-type catalysis, we found that salt additives such as [Bu$_4$N]$^+$Br$^-$or [Ph$_4$P]$^+$Cl$^-$[8c, 23] enhance the activity of catalysts **2a** and **2b**, and that activated chlorobenzenes can be converted (entries 18–21, Table 3). By way of contrast, such salt additives have no influence on the catalytic activity of **3a** and **3b**, and it is not possible to convert chlorobenzenes even under harsh reaction conditions (entry 5, Table 4).

The heterogeneous catalysts **3a** and **3b** are not sensitive to air and moisture, and the reactions can be carried out in air by using technical grade solvents, with no change in selectivities or conversion. The catalysts remain highly active after complete reactions, and upon addition of more substrate catalysis is resumed.

After separation and washing, the heterogeneous catalysts can be reused under the same or similar reaction conditions as for the initial run without any need for regeneration (Scheme 4). The recycling of catalyst **3a** was investigated in detail for the reaction of *p*-bromoacetophenone with styrene (entry 4, Table 4).

The catalyst was used 15 times without detectable loss of activity. The limits of this system can be seen when only 0.02% **3a** are used for the coupling of *p*-bromoacetophenone with *n*-butylacrylate (entry 6, Table 4). In this case, the catalyst can only be recycled six times before the conversion slowly drops down to 80% in the seventh run [total turnover number (TON) = 35500]. On the other hand, noticeable deactivation is displayed in the case of less reactive bromo-

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Table 3. Homogeneous Heck coupling catalysis.[a]

Entry	Aryl halide	Alkene	Catalyst (mol% Pd)[d]	t [h] (T [°C])	Conversion[b] [%]	Yield [%][c] (TON)[e]
1	4-MeCOC$_6$H$_4$Br	CH$_2$=C(H)COO-*n*Bu	**2a** (0.15)	3 (150)	100	> 99 (667)
2	4-MeCOC$_6$H$_4$Br	CH$_2$=C(H)Ph	**2a** (0.15)	5 (150)	100	96 (667)
3	C$_6$H$_5$Br	CH$_2$=C(H)COO-*n*Bu	**2a** (0.15)	16 (160)	96	96 (640)
4	C$_6$H$_5$Br	CH$_2$=C(H)COO-*n*Bu	**2a** (0.15)	60 (160)	100	> 99 (667)
5	C$_6$H$_5$Br	CH$_2$=C(H)Ph	**2a** (0.15)	60 (160)	100	93 (667)
6	4-MeOC$_6$H$_4$Br	CH$_2$=C(H)COO-*n*Bu	**2a** (0.15)	0.17 (170)	72	72 (480)
7	4-MeOC$_6$H$_4$Br	CH$_2$=C(H)COO-*n*Bu	**2a** (0.15)	0.67 (170)	80	80 (533)
8	4-MeOC$_6$H$_4$Br	CH$_2$=C(H)COO-*n*Bu	**2a** (0.15)	2.5 (170)	100	> 99 (667)
9	4-MeOC$_6$H$_4$Br	CH$_2$=C(H)Ph	**2a** (0.15)	12 (160)	90	84 (600)
10	4-MeCOC$_6$H$_4$Br	CH$_2$=C(H)COO-*n*Bu	**2b** (0.15)	4 (160)	100	> 99 (667)
11	4-MeCOC$_6$H$_4$Br	CH$_2$=C(H)Ph	**2b** (0.15)	6 (160)	100	93 (667)
12	C$_6$H$_5$Br	CH$_2$=C(H)COO-*n*Bu	**2b** (0.15)	60 (160)	93	90 (620)
13	C$_6$H$_5$Br	CH$_2$=C(H)Ph	**2b** (0.15)	60 (160)	95	88 (633)
14	4-MeOC$_6$H$_4$Br	CH$_2$=C(H)COO-*n*Bu	**2b** (0.15)	3 (160)	92	92 (613)
15	4-MeOC$_6$H$_4$Br	CH$_2$=C(H)Ph	**2b** (0.15)	3 (160)	86	80 (573)
16	4-MeOC$_{10}$H$_6$Br	CH$_2$=C(H)COO-*n*Bu	**2b** (0.02)	60 (160)	96	96 (4800)
17	4-MeOC$_{10}$H$_6$Br	CH$_2$=C(H)Ph	**2b** (0.02)	60 (160)	89	84 (4450)
18	4-O$_2$NC$_6$H$_4$Cl	CH$_2$=C(H)COO-*n*Bu	**2b** (1)[f]	19 (150)	82	8 (82)
19	4-O$_2$NC$_6$H$_4$Cl	CH$_2$=C(H)COO-*n*Bu	**2b** (1)[f]	72 (150)	99	99 (99)
20	4-MeCOC$_6$H$_4$Cl	CH$_2$=C(H)COO-*n*Bu	**2b** (1)[f]	19 (150)	59	59 (59)
21	4-MeCOC$_6$H$_4$Cl	CH$_2$=C(H)COO-*n*Bu	**2b** (1)[f]	72 (150)	59	59 (59)
22	C$_6$H$_5$Cl	CH$_2$=C(H)COO-*n*Bu	**2b** (1)[f]	30 (160)	0	0 (0)

[a] Reactions were performed in sealed pressure tubes without the exclusion of oxygen/moisture and with non-dried solvents. Yields and product identification were determined by GC-MS. Typical reaction conditions: A molar ratio of 1:1.25:1.5 was used for the aryl halide (10 mmol)/alkene/base [Na(OAc)(anhyd.)]. DMAc (10mL) was used as the solvent. [b] Conversion of the aryl halide with diethylene glycol-*n*-butyl ether as internal standard. [c] GC yield in of the *trans* isomer based on the aryl halide. [d] Based on aryl halide. [e] TON = [moles of coupling product (all isomers)]/(moles of Pd). [f] 20% $[Bu_4N]^+Br^-$ was added.

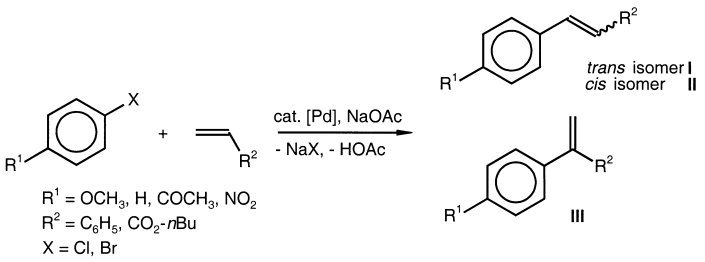
benzene derivatives; nevertheless a total turnover number of about 21 000 is reached for the coupling of bromobenzene with *n*-butyl acrylate (entry 11, Table 4).

The leaching of active species from heterogeneous catalysts into solution is a crucial question in order to identify whether the active centres are attached to the solid support or whether they are dissolved palladium complexes. The observed similarities between the heterogeneously catalyzed reactions and the results obtained using the homogeneous analogues **2a** and **2b** might suggest that the catalyst for these reactions is a dissolved palladium species. To test this, we isolated the catalyst **3a** after 20% conversion (entry 11, Table 4) and

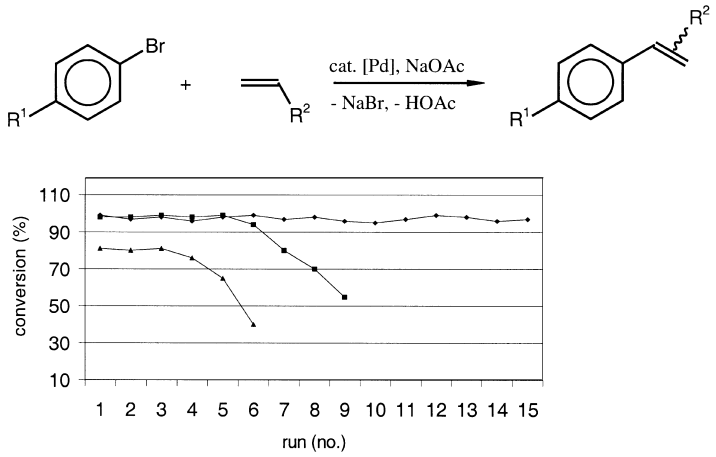
Table 4. Heterogeneous Heck coupling catalysis.[a]

Entry	Aryl halide	Alkene	Catalyst (mol% Pd)[d]	t [h] (T [°C])	Conversion[b] [%]	Yield [%][c] (TON)[e]
1	4-MeCOC$_6$H$_4$Br	CH$_2$=C(H)COO-*n*Bu	**3a** (0.15)	15 (150)	100	> 99 (667)
2	4-MeCOC$_6$H$_4$Br	CH$_2$=C(H)C$_6$H$_5$	**3a** (0.15)	15 (150)	100	95 (667)
3	C$_6$H$_5$Br	CH$_2$=C(H)COO-*n*Bu	**3a** (0.15)	48 (160)	82	82 (547)
4	C$_6$H$_5$Br	CH$_2$=C(H)C$_6$H$_5$	**3a** (0.15)	48 (160)	72	61 (480)
5	4-MeCOC$_6$H$_4$Cl	CH$_2$=C(H)C$_6$H$_5$	**3a** (0.15)	50 (170)	0	0 (0)
6	4-MeCOC$_6$H$_4$Br	CH$_2$=C(H)COO-*n*Bu	**3a** (0.02)	12 (150)	100	> 99 (5000)
7	4-MeOC$_{10}$H$_6$Br	CH$_2$=C(H)COO-*n*Bu	**3a** (0.02)	12 (150)	41	41 (2050)
8	4-MeOC$_{10}$H$_6$Br	CH$_2$=C(H)COO-*n*Bu	**3a** (0.02)	36 (150)	97	97 (4850)
9	C$_6$H$_5$Br	CH$_2$=C(H)COO-*n*Bu	**3a** (0.02)	12 (150)	42	42 (2100)
10	C$_6$H$_5$Br	CH$_2$=C(H)COO-*n*Bu	**3a** (0.02)	24 (150)	71	71 (3550)
11	C$_6$H$_5$Br	CH$_2$=C(H)COO-*n*Bu	**3a** (0.02)	36 (150)	81	81 (4050)
12	4-MeOC$_6$H$_4$Br	CH$_2$=C(H)COO-*n*Bu	**3a** (0.02)	12 (150)	45	45 (2250)
13	4-MeOC$_6$H$_4$Br	CH$_2$=C(H)COO-*n*Bu	**3a** (0.02)	36 (150)	53	53 (2650)
14	4-MeCOC$_6$H$_4$Br	CH$_2$=C(H)C$_6$H$_5$	**3b** (0.02)	60 (150)	100	94 (5000)
15	4-MeCOC$_6$H$_4$Br	CH$_2$=C(H)COO-*n*Bu	**3b** (0.02)	60 (150)	100	> 99 (5000)
16	C$_6$H$_5$Br	CH$_2$=C(H)C$_6$H$_5$	**3b** (0.02)	60 (150)	75	67 (3750)
17	C$_6$H$_5$Br	CH$_2$=C(H)COO-*n*Bu	**3b** (0.02)	60 (150)	82	82 (4100)
18	4-MeOC$_{10}$H$_6$Br	CH$_2$=C(H)C$_6$H$_5$	**3b** (0.02)	60 (150)	82	80 (4100)
19	4-MeOC$_{10}$H$_6$Br	CH$_2$=C(H)COO-*n*Bu	**3b** (0.02)	60 (150)	95	95 (4750)
20	4-MeOC$_6$H$_4$Br	CH$_2$=C(H)C$_6$H$_5$	**3b** (0.02)	60 (150)	38	38 (1900)
21	4-MeOC$_6$H$_4$Br	CH$_2$=C(H)COO-*n*Bu	**3b** (0.02)	60 (150)	42	42 (2100)

[a] Reactions were performed in sealed pressure tubes without the exclusion of oxygen/moisture using non-dried solvents. Yields and product identification were determined by GC-MS. Typical reaction conditions: A molar ratio of 1:1.25:1.5 was used for the aryl halide (10 mmol): alkene: base (Na(OAc)(anhyd.)). DMAc (10mL) was used as the solvent. [b] Conversion of the aryl-halide using diethylene glycol-*n*-butyl ether as internal standard. [c] GC yield of the *trans* isomer based on aryl halide. [d] Based on aryl halide. [e] TON = [moles of coupling product (all isomers)]/(moles of Pd).



Scheme 3. The Heck reaction ("cat. [Pd]" denotes catalytic amounts of **2a**, **2b**, **3a** or **3b**).



Scheme 4. Recycling of the heterogeneous catalyst **3a**. ◆: $R^1 = COMe$, $R^2 = C_6H_5$; $T = 150\,^{\circ}C$; $t = 15$ h; 0.15 % **3a**. ■: $R^1 = COMe$, $R^2 = CO_2$-*n*Bu; $T = 160\,^{\circ}C$; $t = 12$ h; 0.02 % **3a**. ▲: $R^1 = H$, $R^2 = CO_2$-*n*Bu; $T = 160\,^{\circ}C$; $t = 36$ h; 0.02 % **3a**. After the reaction time, methanol was added to the reaction mixture to dissolve the salts and reaction products. The catalyst was collected by filtration and dried in vacuo for further use. Conditions: a molar ration of 1.1:1.25:1.5 was used for the aryl halide (10 mmol)/alkene/base {Na(OAC) (anhydrous)}. DMAc (10 mL) was used as the solvent.

monitored the resulting filtrate under identical reaction conditions for a further 40 hours; no additional conversion was detected upon removal of **3a**. While this method does not allow us to quantify the leaching phenomenon, it clearly demonstrates the absence of active species in solution.

Elemental analysis of the used catalyst **3a** showed the palladium content to be reduced by 0.6 wt % (for a catalyst with 1.0 wt % loading) after the first run. However, elemental analysis of the same catalyst after four runs showed essentially the same palladium content (0.39 % vs. 0.36 %), indicating significant loss of palladium only during the first run. Consistently, a decrease of palladium leaching into the product was observed for recycled catalyst **3a** (38 ppm in the first run vs. 4 ppm in the third run).

Whereas the reaction mechanism of related homogeneous systems was investigated in detail by our group,[8a] the mechanism of the heterogeneously catalyzed rections remains unclear. However, the identical product distributions in homogeneous and heterogeneous reactions indicate that a Pd^0/Pd^{II} cycle is applicable for both. Although we never noticed induction periods, we assume that loss of palladium occurs during the activation step of precatalysts **3a** and **3b** in the initial catalytic run (formation of catalytically active Pd^0 species).

In summary, palladium(II) complexes of *N*-heterocyclic carbenes can successfully be attached to polystyrene-based Wang resin through ether linkages. High activity, easy accessibility and exceptional stability of the immobilized carbene complexes provide an excellent example for a new generation of heterogeneous Heck catalysts. These catalysts are recyclable with very high efficiency and exhibit least leaching for heterogeneous palladium (II) complexes; this is in line with our theoretical investigations on ligand dissociation energies. Detailed investigations focusing on different immobilization techniques and catalytic activity of further coupling reactions are ongoing.

Experimental Section

General procedures: All solvents were used as received as technical grade solvents. *N,N′*-Diimidazolylmethane was prepared according to literature procedures.[24] 4-(Bromomethyl)phenoxymethyl polystyrene (Wang Resin) was obtained from Novabiochem as a 1.00 mmol g^{-1} substitution loading. Other chemicals were obtained from Aldrich and used as received. ^1H and ^{13}C NMR spectra were recorded on a JOEL JNM-GX400 spectrometer in $CDCl_3$, $[D_6]$DMSO and D_2O and referenced to the residual ^1H resonances of the solvents. Solid-state ^{13}C NMR spectra were recorded on a Bruker MSL300 spectrometer equipped with a 4 mm CP-BBMAS probehead and referenced to adamantane as an external standard. The samples were packed in 4 mm ZrO_2 rotors with KeLF caps. Elemental analyses were performed by the microanalytical laboratory at the Technical University of Munich. Melting points were determined in glass capillaries under air. IR spectra were recorded on a FT-IR Perkin–Elmer 1680 spectrometer. Mass spectra were recorded on a Varian MAT311a spectrometer with FAB ionisation (xenon/*p*-nitrobenzylalcohol matrix). GC MS was performed on a Hewlett–Packard 5890 instrument. Yields of catalysis experiments were determined by using diethylene glycol-*n*-butylether as an internal standard.

Synthesis of 1,1′-di(3-hydroxypropyl)-3,3′-methylenediimidazolium dibromide (1a) and 1,1′-di(hydroxyethyl)-3,3′-methylenediimidazolium diiodide (1b): A stirred solution of *N,N′*-diimidazolylmethane (0.50 g, 3.38 mmol) and 3-bromo-1-propanol (0.95 g, 6.80 mmol) or 2-iodo-1-ethanol (1.17 g, 6.80 mmol), respectively, in *iso*-propanol (5 mL) was heated in a sealed pressure tube at 100 °C for 12 h. The *iso*-propanol was removed in vacuo to give a white solid, which was washed with THF (15 mL). Recrystallisation from ethanol gave the products as colourless rods. Yields: 1.18 g (2.77 mmol, 82 %), **1a**; 1.55 g (3.16 mmol, 93 %), **1b**.

Compound 1a: M.p. > 300 °C; ^1H NMR (400 MHz, $[D_6]$DMSO, 25 °C): $\delta =$ 9.77 (s, 2H; NCHN), 8.22 (d, $^3J = 1.84$ Hz, 2H; NCH), 7.97 (d, $^3J = 1.84$ Hz, 2H; NCH), 6.83 (s, 2H; NCH_2N), 4.31 (t, $^3J = 4.09$ Hz, 4H; CH_2OH), 3.41 (t, $^3J = 6.21$ Hz, 4H; CH_2OH), 1.01 (m, 4H; CH_2); ^{13}C NMR (100.53 MHz, $[D_6]$DMSO, 25 °C): $\delta = 138.2$ (NCHN), 123.7 (NCH), 122.4 (NCH), 62.5 (NCH_2N), 56.5 (CH_2), 47.4 (CH_2), 25.9 (CH_2); elemental analysis calcd (%) for $C_{13}H_{22}N_4Br_2O_2$ (426.15): C 36.64, H 5.20, N 13.15; found C 36.89, H 5.16, N 13.29.

Compound 1b: M.p. > 300 °C; ^1H NMR (400 MHz, $[D_6]$DMSO, 25 °C): $\delta =$ 9.42 (s, 2H; NCHN), 7.98 (s, 2H; NCH), 7.80 (s, 2H; NCH), 6.68 (s, 2H; NCH_2N), 4.27 (br, 4H; CH_2OH), 3.61 (br, 4H; NCH_2); ^{13}C NMR (100.53 MHz, $[D_6]$DMSO, 25 °C): $\delta = 138.2$ (NCHN), 124.2 (NCH), 122.4 (NCH), 59.4 (NCH_2), 58.6 (NCH_2N), 52.7 (CH_2OH); elemental analysis calcd (%) for $C_{11}H_{18}N_4O_2I_2$ (492.10): C 26.85, H 3.69, N 11.39; found C 27.07, H 3.74, N 11.68.

Synthesis of [{1,1′-di(3-hydroxypropyl)-3,3′-methylenediimidazolin-2,2′-diylidene}palladium(II) dibromide] (2a) and [{1,1′-di(hydroxyethyl)-3,3′-methylenediimidazolin-2,2′-diylidene}palladium(II) diiodide] (2b): A stirred solution of 1,1′-di(hydroxy-*n*-propyl)-3,3′-methylenediimidazolium dibromide **1a** (380 mg, 0.89 mmol) or 1,1′-di(hydroxyethyl)-3,3′-methylenediimidazolium diiodide **1b** (434 mg, 0.89 mmol), respectively, and $Pd(OAc)_2$ (200 mg, 0.89 mmol) in DMSO (5.0 mL) was heated at 60 °C for 12 hours and then at 130 °C for further 2 hours, during which time the reaction solution had turned pale yellow from being initially orange. The remaining DMSO was then removed in vacuo at 70 °C to give a yellow solid, which was washed with THF (3 mL) to give the products as pure powders. The products were then crystallized by layering saturated DMSO

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solutions with ethanol. Yields: 356 mg (0.67 mmol, 75%), **2a**; 489 mg (0.82 mmol, 92%), **2b**.

Compound 2a: M.p. >300 °C; ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 7.60 (s, 2H; NCH), 7.37 (s, 2H; NCH), 6.29 (s, 2H; NCH$_2$N), 4.14 (br, 4H; CH$_2$OH), 3.38 (br, 4H; NCH$_2$), 1.71 (br, 4H; CH$_2$); ^{13}C NMR (100.53 MHz, [D$_6$]DMSO, 25 °C): δ = 158.8 (C$_{carbene}$), 122.7 (NCH), 121.8 (NCH), 67.5 (NCH$_2$N), 58.2 (CH$_2$), 48.6 (CH$_2$), 25.6 (CH$_2$); IR (KBr): $\tilde{\nu}$ = 3446.0 (OH), 1635.7 cm^{-1} (C=C); FAB MS: *m*/*z* (%): 451 (55) [*M* − Br]$^+$, 369 (100) [*M* − 2Br]$^+$; elemental analysis calcd (%) for C$_{13}$H$_{20}$N$_4$Br$_2$O$_2$Pd (530.56): C 29.43, H 3.80, N 10.56; found C 29.83, H 3.94, N 10.67.

Compound 2b: M.p. 293 °C; ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 7.60 (s, 2H; NCH), 7.36 (s, 2H; NCH), 6.30 (s, 2H; NCH$_2$N), 3.94 (br, 2H; CH$_2$OH), 3.44 (br, 4H; NCH$_2$); ^{13}C NMR (100.53 MHz, [D$_6$]DMSO, 25 °C): δ = 164.45 (C$_{carbene}$), 123.27 (NCH), 121.89 (NCH), 63.75 (NCH$_2$N), 60.90 (CH$_2$), 54.53 (CH$_2$); IR (KBr): $\tilde{\nu}$ = 3422.2 (OH), 1636.6 cm^{-1} (C=C); FAB MS: *m*/*z* (%): 469 (49) [*M* − I]$^+$, 342 (100) [*M*$^+$ − 2I]$^+$; elemental analysis calcd (%) for C$_{11}$H$_{16}$I$_2$N$_4$O$_2$Pd · C$_2$H$_6$OS (674.63): C 23.14, H 3.29, N 8.30; found C 23.21, H 3.22, N 8.38.

Immobilisation of 2a and 2b on 4-(bromomethyl) phenoxymethyl polystyrene

Preparation of catalysts 3a and 3b: A solution of **2a** (100 mg, 0.19 mmol) or **2b** (113 mg, 0.19 mmol), 4-(bromomethyl)phenoxymethyl polystyrene (188 mg, *c*(Br) = 1.00 mmol g^{-1}), di-*iso*-propylethylamine (73 mg, 0.57 mmol) and CsI (15 mg, 0.06 mmol) in DMF (4.0 mL) was stirred for 48 h at room temperature. The pale yellow beads were collected and washed with *N*,*N*-dimethyl acetamide (DMAc; 3 × 6 mL) and MeOH (2 × 10 mL), and dried in vacuo.

Compound 3a: ^{13}C NMR (solid state, 300 MHz, ν_r = 10 kHz, 25 °C): δ = 160.0 (br, C$_{carbene}$), 69.5 (br, NCH$_2$N); IR (KBr): $\tilde{\nu}$ = 3443.6 (OH), 1635.6 cm^{-1} (C=C); elemental analysis calcd (%) for a loading of 1.0% palladium: N 0.53; found Pd 1.0, N 0.59.

Compound 3b: IR (KBr): $\tilde{\nu}$ = 3448.3 (OH), 1636.5 cm^{-1} (C=C); elemental analysis calcd (%) for for a loading of 1.1% palladium: N 0.58; found Pd 1.1, N 0.62.

General procedure for Heck catalysis: The reactions for Heck coupling studies were typically conducted as follows: The aryl halide (1.0 equiv, 10 mmol), alkene (1.2 equiv, 12 mmol), base (1.5 equiv, 15 mmol), salt additive (if used), internal standard (100 mg diethylene glycol-*n*-butyl-ether) and catalyst were added to a thick-walled 17 cm Ace pressure tube; the solvent (10 mL) and a magnetic stirrer were added. The tube was sealed with an o-ringed Teflon cap and heated to the appropriate temperature of the experiment. The reaction progress was monitored by the removal of a small aliquot of the reaction mixture, which was analyzed by GC-MS. The pressure tubes were then cooled to room temperature; a small aliquot of the reaction mixture was taken for GC-MS analysis of the reaction. Products were identified by comparison with authentic samples. In case of heterogeneous catalysts **3a** and **3b**, methanol was added to the reaction mixture to dissolve all salts and reaction products. The catalyst was collected by filtration and dried in vacuo for further use.

Computational details: The geometries of the model complexes were optimized at the BP86[25] level of theory in combination with the DZVP basis set[26] on all atoms. This basis set, in combination with the A1 set of auxiliary fitting functions for the density and the exchange-correlation potential, was designed to reduce the basis set superposition error (BSSE). Otherwise, no efforts were made to correct for the basis set superposition problem, which tends to cancel with the basis set incompleteness error for medium-sized basis sets. The accuracy of this method has been shown in a previous study.[27] The resulting energy-minimized structures were characterized by calculating the eigenvalues of the force-constant matrix. All calculations were carried out with the DGauss 4.0 program.[28]

X-ray diffraction studies for compound 2b: All X-ray data were collected on a Nonius Kappa CCD detection system at 173 K with graphite-monochromated Mo$_{K\alpha}$ radiation. A total number of 15948 reflections were measured and 4187 unique reflections (R_{int} = 0.0363) were used in the full-matrix least-squares refinement. The intensities of the reflections were corrected for absorption effects.[29] The structure was solved by direct methods[30] and refined by full-matrix least-squares calculations with SHELXL-97.[31] All heavy atoms of the compound were refined with anisotropic temperature factors. All hydrogen atoms were found from the electron-density maps and were refinded. Crystallographic data and experimental details of compound **2b** are given in Table 5. Selected structural parameters are given in Table 2. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-135476. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Table 5. Crystal data and details of the structure determination for compound **2b**.

formula	C$_{11}$H$_{16}$I$_2$N$_4$O$_2$Pd · C$_2$H$_6$OS
M_w	674.64
crystal system	triclinic
space group	$P\bar{1}$ (No. 2)
a [Å]	8.8260(3)
b [Å]	9.0680(3)
c [Å]	13.5670(4)
α [°]	107.4390(17)
β [°]	94.6290(15)
γ [°]	93.9990(16)
V [Å^3]	1027.49(6)
Z	2
ρ_{calcd} [g cm^{-3}]	2.181
μ [mm^{-1}]	4.0
crystal size [mm]	0.20 × 0.13 × 0.10
T [K]	173
λ [Å]	0.71073
θ min/max	2.3/26.4
F(000)	640
total reflections	15948
unique reflections	4187
observed reflections [$I > 2\sigma(I)$]	3789
$R_1(F_o)$[a]	0.0321
$wR_2(F_o^2)$[b]	0.0822
goodness of fit[c]	1.05
$\Delta\rho$ min/max [e Å^{-3}]	−1.46/1.31

[a] $R_1 = \Sigma\,||F_o| - |F_c||/\Sigma\,|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. [c] Goof = $\{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$.

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