Iridium(I) Complexes Containing the η^1-N-Bonded Indolyl Ligand

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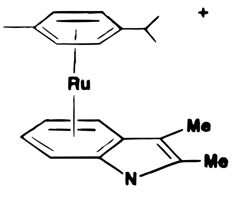
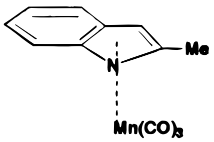
Summary: The reaction of Ir(CO)(Cl)(PPh$_3$)$_2$ with indolyllithium reagents has led to the formation of σ-N-coordinated indolyl derivatives of the formula trans-Ir(CO)(PPh$_3$)$_2$(indolyl), ***1a****, when the indolyl ligand is unsubstituted, and the 2,3-Me$_2$indolyl derivative* ***1b****. Complex* ***1b*** *has been characterized by an X-ray diffraction study. The indolyl ligand functions primarily as a σ-donor to the metal ion, and the Ir−N bond is stable to protic acid. Reaction with triflic acid results in protonation at the 3-position of the heterocycle and formation of an indolenine complex.*

Introduction

As part of a program to study the reactivity of coordinated nitrogen heterocycles, we have recently characterized new indolyl complexes of ruthenium(II) of the formula [(cymene)Ru(indolyl)]$^+$.[1] ^{13}C NMR data suggested that the indolyl ligand was coordinated through the carbocyclic ring, and an X-ray diffraction study of the 2,3-Me$_2$indolyl derivative confirmed the η^6-bonding mode of the ligand, **I**. A previous structural study of an indolyl complex of Mn(I), [(indolyl)Mn(CO)$_3$], had established that the heterocycle in this complex was coordinated through the anionic, electron rich nitrogen ring in an η^5 interaction, **II**.[2] We are interested in understanding the factors which dictate η^5- or η^6-coordination of the indolyl ligand and in comparing the reactivities of these bonding modes. We have, therefore, begun to explore other potential synthetic routes to η^5-indolyl complexes.



I

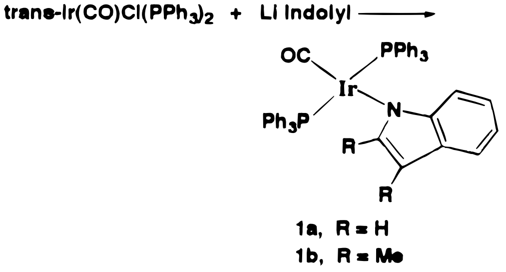


II

The reaction of Ir(CO)Cl(PPh$_3$)$_2$ with NaCp or with substituted Cp anions has been reported to form η^5-Cp′Ir(CO)PPh$_3$ in good yield.[3−5] Since η^5-pyrrolyl analogues of several Cp derivatives are known,[6] we have explored the reaction of this Ir(I) complex with pyrrolyl and indolyl reagents. In contrast to the Cp reagents, the indolyl salts reacted with the iridium complex to form η^1-N-bonded derivatives. We report here the characterization data and some reactivity studies of these new indolyl complexes of Ir(I).

Results and Discussion

Reactions of Ir(CO)Cl(PPh$_3$)$_2$ with Indolyl and Indole Ligands. The complex Ir(PPh$_3$)$_2$(CO)Cl was reacted with 2 equiv of indolyllithium in refluxing toluene for 1 day. The reaction conditions were similar to a procedure reported for the synthesis of the η^5-Cp derivatives.[3] A light green product was isolated from the reaction in 81% yield, and spectroscopic data suggested that its formulation was IrCO(PPh$_3$)$_2$(η^1-indolyl), **1a**, eq 1. A parent ion for this composition was observed in the FAB mass spectrum at *m/e* 862. ^{1}H, ^{13}C, and ^{31}P NMR data confirmed that the product contained two equivalent phosphines and an indolyl ligand (see the Experimental Section). In previous studies of [(cymene)Ru(indolyl)]$^+$, ^{13}C chemical shifts for the carbocyclic ring were found between 82 and 90 ppm, shifted significantly upfield from the free ligand. The upfield shifts appeared to be quite diagnostic of an η^6-coordinated ligand.[1] In the ^{13}C spectrum of **1a**, resonances for the indolyl carbons, with the exception of C2, occurred between 100−119 ppm; these shifts are similar to those reported for the free indole ligand.[7] However, the chemical shift for C2 in **1a** was observed at 144 ppm, compared to 124 ppm for the free ligand. A similar downfield shift for the α-C has been observed previously for N-bonded indolyl derivatives of Re(I)[8] and of Ta(V).[9]



(1)

[⊗] Abstract published in *Advance ACS Abstracts,* February 15, 1997.

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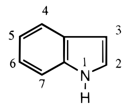

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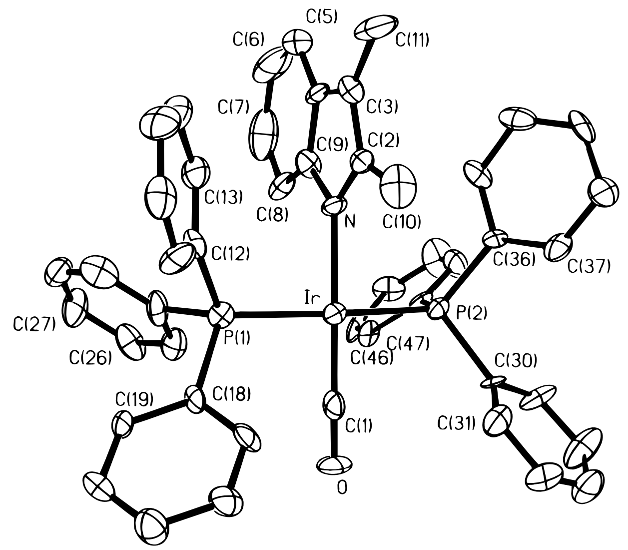

Figure 1. Perspective drawing and numbering scheme for $Ir(PPh_3)_2(CO)(2,3\text{-}Me_2indolyl)$, **1b**.

The infrared spectrum of **1a** showed a strong CO stretch at 1956 cm^{-1}. The frequency is similar to that observed for $Ir(CO)(PPh_3)_2Cl$ (1961 cm^{-1}).[10] Although the indolyl ligand is formally an amide anion, there appears to be little L−M back-bonding involving the nitrogen lone pair, which is not localized on nitrogen but delocalized over the aromatic heterocycle. Closely related amide derivatves $Ir(CO)(PPh_3)_2(NHAr)$ have been reported recently.[11] In these complexes, the CO stretch was observed between 1940 and 1944 cm^{-1}, indicating that a greater degree of electron density is donated from the amide ligands.

The lithium salt of 2,3-dimethylindole was also reacted with the starting iridium complex. We wished to determine whether the methyl substituents would enhance the electron donating character of the five-membered ring enough to favor π-coordination. However, the product obtained from this reaction displayed spectroscopic features similar to those of **1a** and was formulated as $Ir(CO)(PPh_3)_2(\eta^1\text{-}2,3\text{-}Me_2indolyl)$, **1b**. In order to prevent the σ-coordination of the indolyl nitrogen and promote a π-bonding mode, we have attempted reactions of the Ir(I) reagent with neutral N−Me−indole. The reaction solution containing 2 equiv of the indole ligand was refluxed in toluene for 2 days, but only starting reagents were recovered, and no evidence for indole coordination was observed. A similar lack of reactivity was observed for the reaction of $[Ir(PPh_3)_2CO(CH_3CN)]^+$ [12] with N−Me−indole.

X-ray Diffraction Study of 1b. Single crystals of **1b** were grown by slow diffusion of EtOH into a diethyl ether solution. The complex crystallized in the space group $P2_12_12_1$ with four molecules per unit cell. A perspective drawing of the molecule is shown in Figure 1, and selected bond distances and angles are given in Table 1. The structure shows the expected square planar coordination geometry with *trans*-PPh_3 ligands, one carbonyl, and a σ-N-bonded indolyl ligand. The nitrogen atom of the 2,3-Me_2indolyl ligand maintains a planar geometry, with the sum of the Ir−N−C and C−N−C angles equal to 360°. The plane of the ligand is oriented nearly perpendicular to the plane of the Ir−ligand bonds, with a dihedral angle of 92.3°. The metal−ligand bond distances in **1b** are very similar to those reported for the related Ir(I) complex $Ir(PPh_3)_2(CO)(NHpC_6H_4Me)$.[11a] X-ray diffraction studies of N-bonded indolyl complexes have been reported previously for $CpRe(NO)(PPh_3)(3\text{-}Etindolyl)$,[8] $(\eta^5\text{-}C_4Me_4N)TaMe_3(indolyl)$,[9] and for $Ir(H)(Cl)(PMe_3)_3(indolyl)$.[13] Bond distances and angles for the nitrogen heterocycles are similar in the structures and do not differ significantly from those of free indole.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for $Ir(CO)(PPh_3)_2(\eta^1\text{-}2,3\text{-}Me_2indolyl)$, 1b

Ir−C(1)	1.782 (14)	C(3)−C(4)	1.42 (2)
Ir−P(1)	2.329 (3)	C(4)−C(5)	1.39 (2)
Ir−P(2)	2.316 (3)	C(5)−C(6)	1.30 (2)
Ir−N	2.080 (10)	C(6)−C(7)	1.49 (2)
O−C(1)	1.18 (2)	C(7)−C(8)	1.41 (2)
N−C(9)	1.37 (2)	C(8)−C(9)	1.42 (2)
N−C(2)	1.39 (2)	C(4)−C(9)	1.41 (2)
C(2)−C(3)	1.41 (2)		
C(1)−Ir−N	178.3 (6)	C(1)−Ir−P(2)	90.5 (4)
N−Ir−P(2)	89.3 (3)	C(1)−Ir−P(1)	90.9 (4)
N−Ir−(P1)	89.2 (3)	P(2)−Ir−P(1)	175.85 (13)
C(9)−N−C(2)	105.2 (11)	C(9)−N−Ir	127.8 (9)
C(2)−N−Ir	127.0 (9)	O−C(1)−Ir	177.1 (12)

Reactions of $Ir(CO)(indolyl)(PPh_3)_2$. Reaction with Protic Acid. Early studies of Vaska's compound and related derivatives established that addition of a strong acid led to protonation and a formal oxidation of the metal center.[14] In studies of the amide complex $Ir(CO)(PEt_3)_2(NH(\textit{tert}\text{-butyl}))$, the amide ligand was ultimately removed from the metal ion even in reactions with weak acids such as phenylacetylene.[15] The reaction of **1b** with triflic acid was monitored by NMR spectroscopy. Unlike the basic amide complex described above, the metal−nitrogen bond of **1b** was quite stable toward strong acid. Free 2,3-dimethylindole was observed in the spectrum in only ca. 5% yield. The major product, which was isolated and characterized by spectroscopic data, was proposed to be the Ir−indolenine derivative resulting from protonation at the 3-position of the indolyl ligand, eq 2. The formulation of the product complex, **2**, was consistent with the ^1H NMR and COSY spectra. A quartet at 2.55 ppm was assigned to H(3), and the methyl resonance at the 3-position appeared as a doublet shifted upfield to 0.68 ppm. A similar protonation of a coordinated indolyl ligand has been characterized previously in studies of diastereoselective electrophilic additions to $CpRe(PR_3)NO(indolyl)$.[8] A previously reported complex containing the indolenine ligand, *trans*-$Pd(Cl)_2(indolenine)_2$, has been characterized by an X-ray diffraction study.[16] In this system, the ligand was obtained by rearrangement of neutral indole in its reaction with $PdCl_4^{-2}$.

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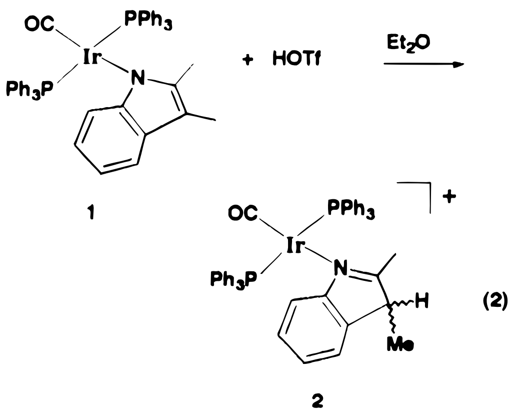
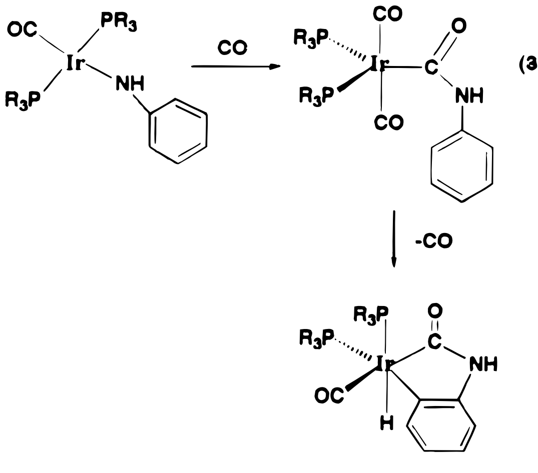


(2)

Reaction with Hydride Reagents. The η^6-coordination of indole ligands to metal ions is known to activate the ligand toward nucleophilic attack,[17] and in theory, the σ-coordination of indolyl to transition metals could also activate the ring toward reactions with nucleophiles. However, in the Ir(I) systems prepared here, the spectrocopic data as well as the reaction with acid, described above, suggest that the η^1-indolyl ligand is quite electron rich. Consistent with this characterization, the reaction of **1a** with hydride nucleophiles did not provide any evidence for nucleophilic addition to the indolyl carbon atoms. For example, reaction with $NaBH_4$ at room temperature resulted in the displacement of the indolyl ligand, and the formation of a mixture of iridium hydride products. On the basis of the ^{1}H NMR data, isomers of $Ir(PPh_3)_2(CO)(H)_3$, which have been observed previously in reactions of $Ir(PPh_3)_2(CO)Cl$ with $NaBH_4$,[18] appear to be present in this product mixture, as well as other unidentified hydrides.

Attempted Reaction with Carbon Monoxide. Ir(I) arylamide complexes have been reported to undergo an insertion reaction with carbon monoxide to produce carbamoyl derivatives. In most cases the carbamoyl ligand was found to undergo a further cyclometalation reaction, eq 3.[11,14] In a further comparison of the properties of the analogous indolyl complex, we have attempted to react **1a** with excess carbon monoxide. However, no insertion product was observed at room temperature after reaction with ca. 3 atm of CO over a period of 18 h. The difference in reactivity again reflects the delocalization of the nitrogen lone pair over the aromatic ring and a lower resonance stabilization available for a carbamoyl product. Like the parent Ir(I)−Cl derivative,[19] **1a** did not form an isolable CO adduct at ambient conditions; only the starting reagent was recovered upon work-up.



(3)

Conclusions

The reactions of $Ir(CO(Cl)(PPh_3)_2$ with indolyl salts resulted in the formation of N-bonded indolyl derivatives of the formula *trans*-$Ir(CO)(PPh_3)_2$(indolyl). No evidence for π-bonded indolyl products was detected in these systems. The new derivatives synthesized in this study were found to be stable complexes which have potential for further modification of the indolyl molecule; for example, the indolyl ligand was susceptible to electrophilic addition by strong acid at the 3-position of the ring, and the resulting indolenine cation has been isolated and characterized.

Experimental Section

Materials. The complex $Ir(CO)Cl(PPh_3)_2$ was purchased from Strem, and indole reagents were obtained from Aldrich. Indolyllithium reagents were prepared by treatment of indoles with an equimolar amount of *n*-BuLi in Et_2O or hexane solution. The resulting salts were isolated by filtration and stored under nitrogen at −30 °C. The solvents toluene, tetrahydrofuran, and diethyl ether were distilled from Na/benzophenone. Reactions were carried out under N_2 using standard Schlenk line techniques.

***trans*-Ir(PPh₃)₂(η^1-indolyl)(CO), 1a.** A solution of indolyllithium (0.035 g, 0.280 mmol) and $Ir(PPh_3)_2(CO)Cl$ (0.22 g, 0.28 mmol) in 60 mL of toluene was refluxed at 100 °C for 1 day. The solvent was evaporated, leaving a green solid, which was extracted with 80 mL of Et_2O. The solution was filtered, and the filtrate was evaporated to give a light green solid. Yield: 0.196 g (81.0%). ^{1}H NMR ($CDCl_3$):[20] δ 7.24−7.36 (m, 18H, PPh_3), 7.12−7.19 (m, 13H, PPh_3 and H7), 7.02 (d, H4, $J = 8$), 6.50, 6.34 (2t, H5 and H6, $J = 8$), 6.05, 5.87 (2d, H2 and H3, $J = 3$). ^{13}C NMR ($CDCl_3$): δ 178.6 (t, $J = 11$, Ir−CO); 144.2 (s, ind C2); 134.1, 131.3 (s, ind quat C); 134.2 (t, $J = 6$, *o*-C of PPh_3); 130.1 (s, *p*-C of PPh_3); 131.7 (t, $J = 26$, *i*-C of PPh_3); 127.9 (t, $J = 5$, *m*-C of PPh_3); 118.6, 117.0, 115.8, 115.4 (s, ind C4-C7); 100.8 (s, ind C3). ^{31}P NMR ($CDCl_3$): δ 23.17. MS (FAB$^+$): *m/e* 862 (861 calcd for M − e), 773 (M + CO − indolyl), 745 (M − indolyl), 715 (717 calcdd for $Ir(PPh_3)_2$). IR (KBr, cm^{-1}): 1956 (s, ν_{co}), 1434 (m), 1262 (m), 1096 (m), 820 (m). The product was found to be hygroscopic, and NMR data confirmed the presence of water in samples which were exposed to air. Anal. Calcd for $C_{45}H_{36}NOIrP_2{\cdot}3H_2O$: C, 59.07; H, 4.63; N, 1.53. Found: C, 59.25; H, 4.45; N, 1.65.

***trans*-Ir(PPh₃)₂(η^1-2,3-Me₂indolyl)(CO), 1b.** (2,3-Dimethylindolyl)lithium (0.025 g, 0.025 mmol) and *trans*-$Ir(PPh_3)_2(CO)Cl$ (0.092 g, 0.012 mmol) were combined in 30 mL of toluene. The yellow solution was refluxed at 100 °C for 3 days. The solvent was removed under vacuum, leaving a yellow solid, which was extracted with 40 mL of Et_2O. The solution was filtered, and the filtrate was evaporated to give a greenish-yellow solid. ^{1}H NMR ($CDCl_3$): δ 7.25−7.32 (m, 18H, PPh_3), 7.14−7.20 (m, 12H, PPh_3), 7.12 (d, H7, $J = 8$), 7.01 (d, H4, $J = 8$), 6.52, 6.34 (2 t, H5 and H6, $J = 7$), 1.75 (s,

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[20] Indolyl resonances are tentatively assigned on the basis of coupling patterns and by analogy to chemical shift patterns of other indolyl complexes[8,9,13] and of the free ligands.

Table 2. Crystal Data for $Ir(CO)(PPh_3)_2(2,3\text{-}Me_2indolyl)$, 1b

form	$C_{47}H_{40}NOP_2Ir$
mol wt (amu)	888.94
cryst syst	orthorhombic
unit cell dimensions	
a(Å)	10.752(2)
b (Å)	15.303(3)
c (Å)	23.609(5)
β (deg)	90
vol, Å^3	3884.6 (14)
space group	$P2_12_12_1$
Z	4
density, calcd, g/cm^3	1.520
λ (Mo Kα, Å)	0.710 73
temp (K)	175(2)
scan type	modified *ω* scan
θ range (deg)	1.59−27.53
independent reflns	5869
refls obsd	4161
abs corr	XABS2[a]
R^b	0.0608
$R_w{}^c$	0.1096
GOF	0.982
largest peak in final diff map e$^-$/Å^3	1.655 and −1.131

[a] Parkin, S. R.; Moezzi, B.; Hope, H. *J. Appl. Crystallogr.* **1995**, *28*, 53. [b] $R = R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum w(F_o{}^2)^2]^{1/2}$.

3H, $NCCH_3$), 1.47 (s, 3H, $NC{=}CCH_3$). ^{31}P NMR ($CDCl_3$): *δ* 22.65. MS (CI^-): *m/e* 627 (M − PPh_3), 365 (M − $2PPh_3$).

X-ray Diffraction Study of *trans*-$Ir(PPh_3)_2(\eta^1\text{-}2,3\text{-}Me_2indolyl)(CO)$. Complex **1b** was crystallized by slow diffusion of EtOH into an Et_2O solution of the compound. Crystals formed in the space group $P2_12_12_1$. The structure was solved by direct methods on a Nicolet R3 Nova diffractometer using the SHELXTL program package. A least-squares refinement based on F^2 was performed. Details on the crystal data, experimental conditions, and solution and refinement information are given in Table 2.

$[(\eta^1\text{-}2,3\text{-}Me_2indolenine)Ir(PPh_3)_2(CO)][OTf]$, 2. To a yellow solution of **1b** (0.052 g, 0.058 mmol) in 30 mL of Et_2O was added triflic acid (0.040 mL, 0.45 mmol). After 90 min, a yellow precipitate was present. The clear supernatant was decanted, and the yellow solid was washed with Et_2O. Yield: 0.0472 g, 78%. ^1H NMR ($CDCl_3$): (assignments are based on COSY NMR spectroscopy) *δ* 7.65 (d, H7, *J* = 8), 7.43−7.55 (m, 18H, PPh_3), 7.34−7.43 (m, 13H, H4 and 12H of PPh_3), 7.07−7.16 (m, 2H, H5 and H6), 2.55 (q, 1H, H3), 2.06 (s, 3H, $N{=}CCH_3$), 0.682 (d, 3H, *J* = 7.8, $N{=}C{-}CCH_3$). ^{31}P NMR ($CDCl_3$): 25.40 (AB pattern). ^{13}C NMR ($CDCl_3$): 191.1, 190.1 (br, Ir−CO and C=N); 150.3, 138.9 (s, ind quat C); 133.9, 131.6, 128.9 (br, PPh_3); 130.7, 127.8, 127.3, 122.9 (s, ind, C4−C7); 118.3 (br, OTf); 50.8 (s, *C*HMe); 20.0 (s, Me); 12.3 (s, Me). IR ($CHCl_3$): 2000 cm^{-1} (ν_{CO}). MS (FAB^+): *m/e* 890 (M − OTf), 715 (717 calcd for $Ir(PPh_3)_2$). MS (FAB^-): *m/e* 1188 (M + OTf). Anal. Calcd for $C_{48}H_{41}O_4SF_3IrP_2N$: C, 55.49; H, 3.98; N, 1.35. Found: C, 55.39; H, 3.81; N, 1.07.

Reaction of 1a with $NaBH_4$. Complex **1a** (0.0389 g, 0.0452 mmol) and $NaBH_4$ (0.040 g, 0.11 mmol) were dissolved in 30 mL of THF and stirred at room temperature for 22 h. The solvent was evaporated, and the solids were extracted with Et_2O, forming a yellow solution. The solution was filtered, and the solvent was evaporated. In the NMR spectrum of the product, no resonances for Ir-coordinated indolyl were observed. The iridium products included several hydride resonances. ^1H NMR ($CDCl_3$): −10.14 (dt, *mer*-$IrH_3(PPh_3)_2(CO)$), −10.59 (tt, *mer*-$IrH_3(PPh_3)_2CO$),[18] −11.44 (dd, *fac*-$IrH_3(PPh_3)_2$-(CO)), −10.20 (dt, *fac*-$IrH_3(PPh_3)_2(CO)$.[18] Unidentified resonances were also observed at −10.80 (AB), −11.22 (br), −11.68 (br).

Attempted Reaction of *trans*-$Ir(PPh_3)_2(\eta^1\text{-}indolyl)(CO)$, 1a, with CO. Complex **1a** (0.037 g, 0.042 mmol) was dissolved in 30 mL of Et_2O to form a green-yellow solution. The solution was transferred to a high pressure flask, and 3 atm of carbon monoxide was added at room temperature. The tube was sealed and allowed to stir for 18 h. The solvent was then evaporated, leaving a yellow solid. The ^1H NMR spectrum ($CDCl_3$) showed only resonances for the starting material.

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Supporting Information Available: Tables of the details of data collection, solution and refinement, atomic coordinates, bond distances, bond angles, and positional and thermal parameters for **1b** (10 pages). Ordering information is given on any current masthead page.

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