Reactivity of Dimesitylfluorenylidenegermane with Unsaturated Nitrogen Compounds

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Dimesitylfluorenylidenegermane (1) reacts with ethylbenzylideneamine (PhCH=NEt) to give, according to a [2 + 2] cycloaddition, the very thermally stable four-membered-ring germaazetidine 2. In contrast, imines with a NH function, such as (diphenylmethylidene)amine (Ph_2C=NH), react only as protic reagents. A [2 + 4] cycloaddition is observed with azobenzene, affording 5, which slowly aromatizes to 6 or thermally rearranges to give the [2 + 2] cycloadduct germadiazetidine 7. In the case of nitrosobenzene, only the germanone dimer 17 and imine 9 have been observed, probably via the preliminary formation of transient four-membered heterocycle 15.

Introduction

During the last few years there has been great interest in the chemistry of unsaturated compounds M=M′ (M, M′ = group 13–15 elements particularly).[1]

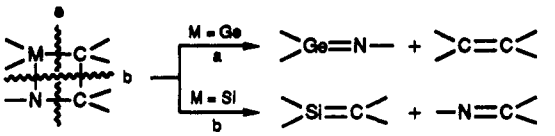
Such derivatives, which for a long time have only been evidenced by trapping reactions, have recently been kinetically stabilized; thus, their reactivity has been studied toward a large number of unsaturated compounds. Nevertheless, very little is known about their chemical behavior toward imines and azo and nitroso compounds; only reactions between some of these derivatives and a silene, >Si=C<, have been described by Wiberg.[2]

In a continuation of our investigations of heavier homologues of alkenes, we report here our results about the reactivity of dimesitylfluorenylidenegermane (1)[3] with ethylbenzylideneamine, (diphenylmethylidene)amine, azobenzene, and nitrosobenzene.

Results and Discussion

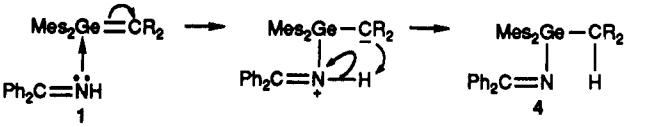
(1) Imines. Ethylbenzylideneamine (PhCH=NEt) reacts with germene 1, but only after heating for 12 h at 140 °C in a sealed tube, to afford the 2-germaazetidine 2, by a [2 + 2] cycloaddition. The formation of 2 can be explained through the ionic interaction of the lone pair of nitrogen with the germanium atom at the beginning of the reaction to form a zwitterion type intermediate that might smoothly give the final product; we have never observed in this reaction the [2 + 4] cycloadduct 3. However, the preliminary formation of this heterocycle, followed by its isomerization to 2, is not excluded: the isomerization six-membered ring → four-membered ring has been postulated by Wiberg in silaoxetanes[2b] (Scheme I).

Only one isomer, with probably the phenyl and ethyl groups in trans positions, is observed by NMR spectroscopy. Heterocycle 2 is the first thermally and photolytically stable four-membered ring of this type. Its great stability is probably due to the very large steric hindrance caused particularly by mesityl groups on germanium; less hindered germaazetidines obtained by other routes undergo a [4] → [2] + [2] decomposition[4] with formation of the corresponding germanimines and alkenes (route a). Note that, in contrast, the silaazetidine isologues give only the cycloreversion leading to the starting silenes and imines[2] (route b). In mass spectrometry, we have observed the same type of [4] → [2] + [2] cycloreversion as for

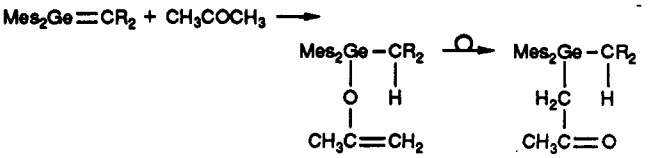


silaazetidine, leading to the starting germene and imine, which are among the most important fragments. We have never observed in this case the decomposition according to route a.

In the reaction between (diphenylmethylidene)amine (Ph_2C=NH) and 1 we have only observed the formation of 4. As 1 is very reactive toward protic reagents,[3a] it reacts, as expected, more easily with the NH bond to give 4 than with the imine function to afford the [2 + 2] or the [2 + 4] adduct; in this last reaction, we can also propose the formation of a zwitterionic intermediate resulting from the nucleophilic attack of the nitrogen atom at the electrophilic germanium, in agreement with the polarity $Ge^{\delta+}$ = $C^{\delta-}$ of the germanium–carbon double bond:[3]



Note that, although ketones very easily give [2 + 2] cycloadducts with 1,[5] acetone also reacts exclusively as a protic reagent, by the enolic form:[5]



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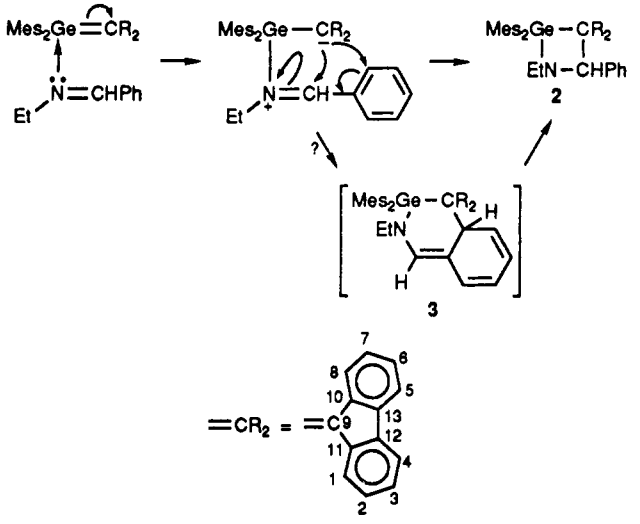
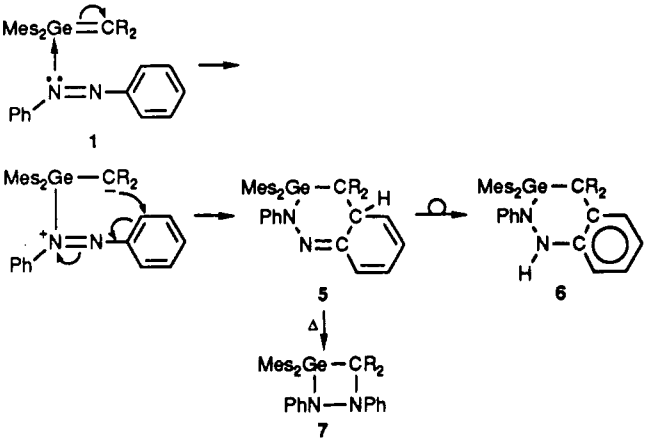
Scheme I



Scheme II



(2) Azobenzene. A completely different reaction occurs with azobenzene. After 5 h in refluxing Et_2O there was a [2 + 4] cycloaddition leading to the six-membered-ring derivative **5**; as in the reactions with imines, the formation of a zwitterionic intermediate seems probable. **5** has been clearly characterized by its physicochemical data. In its proton NMR spectrum, it presents six different signals for the methyls of mesityl groups: due to the high steric hindrance, the rotation of mesityl groups is hindered, and the ortho methyls are inequivalent. After about 10 days at room temperature, **5** quantitatively rearranges to **6**; the driving force of this rearrangement is of course the aromatization, which could be catalyzed by traces of oxygen.[6]

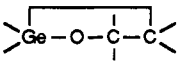
The mass spectrometry of **5**, carried out at 130 °C, is rather surprising for a six-membered-ring derivative: besides the molecular peak (M, *m/e* 658), we have observed two types of fragmentation generally characteristic of a four-membere -ring compound (see Experimental Section); thus, it seems that, at this temperature in the spectrometer, **5** rearranges to the germadiazetidine **7** (Scheme II).

Heating **5** in a sealed tube at 100 °C for 5 h proves the isomerization **5** → **7**. Although **7** has not been isolated in a pure state, its formation was proved by NMR spectroscopy and by its decomposition products characteristic of such a heterocycle: further heating at 150 °C with small amounts of water leads to azobenzene, **12**, and **13** along with minor unidentified products. The two germylated compounds have been obtained in pure form by a careful fractionated recrystallization (Scheme III).

The formation of these compounds can be explained by [4] → [2] + [2] cycloreversions leading to germene **1** and azobenzene (route a) and germanimine **8** and imine $PhN{=}CR_2$ (**9**) (route b). Addition of water to the double bond of **1** leads to **11**; further reaction of **11** with **1** affords **13**. Such formation of **13** from **1** and water has already been proved.[5] Formation of **12** could be explained by the reaction of **11** with germanimine **8** or of **10** with germene **1**.

This mechanism involving the preliminary formation of germene **1** and germanimine **8**, which corresponds to the decomposition observed in mass spectrometry, seems probable. However, other mechanisms leading to these different compounds cannot be excluded: for example, the preliminary cleavage of the Ge–N bond of the four-membered ring **7**, followed by rearrangements, as water easily cleaves standard Ge–N bonds. Due to the very large steric hindrance, however, we can postulate a probable important inertness of this bond toward hydrolysis. For example, in the four-membered-ring germaoxetane Mes_2GeCR_2CHPhO, which is substituted by the same groups on germanium and carbon as **7**, the Ge–O bond was only cleaved by hydrofluoric acid,[5] although classical Ge–O bonds are sensitive to water.[7]

(3) Nitrosobenzene. Reaction of **1** with nitrosobenzene affords only the imine **9** and 2,4-digerma-1,3-dioxetane **17**; the formation of such compounds probably involves the preliminary formation of four-membered heterocycle **15** followed by a classical [4] → [2] + [2] decomposition (Scheme IV). Such decompositions leading to germanones are well-known from other four-membered heterocycles such as 2-germaoxetanes[1c]



although **15** is probably directly obtained from **1** and nitrosobenzene (route a), the preliminary formation of six-membered-ring heterocycle **14**, followed by its rapid isomerization, as in the case of azobenzene, cannot be completely ruled out.

Experimental Section

General Procedures. As solutions of germene **1** are highly air- and moisture-sensitive, all the experiments were performed under argon or nitrogen with carefully dried and deoxygenated solvents. ^1H NMR spectra were recorded on a Bruker AC 80 instrument at 80.1 MHz or on a Bruker AM 300 WB spectrometer at 300.1 MHz and ^{13}C NMR spectra on a Bruker AC 200 instrument at 50.3 MHz (TMS internal standard). Mass spectra were measured on a Nermag R10 010 spectrometer (EI). Melting points were determined on a Reichert apparatus, and elemental analyses were done by the "Service de microanalyse de l'Ecole de Chimie", Toulouse, France. Carbons of fluorenyl are numbered C_1–C_{13}.

Reaction of 1 with Ethylbenzylideneamine. A mixture of ethylbenzylideneamine (0.28 g, 2.1 mmol), of germene **1** (1.00 g, 2.1 mmol) and of Et_2O (5 mL) was heated in a sealed tube for 12 h at 140 °C. After elimination of the solvent in vacuo, crude **2** is recrystallized in pentane to afford 1.03 g (75%) of white crystals, mp 190–191 °C. ^1H NMR (C_6D_6, 300 MHz, 25 °C): δ 1.23 (t, $^3J(HH)$ = 7.1 Hz, 3 H, CH_3CH_2), 2.03 (s, 3 H, *p*-Me), 2.04 (s, 3 H, *p*-Me), 2.06 (s, 6 H, *o*-Me), 2.27 (broad s, 6 H, *o*-Me), 3,33

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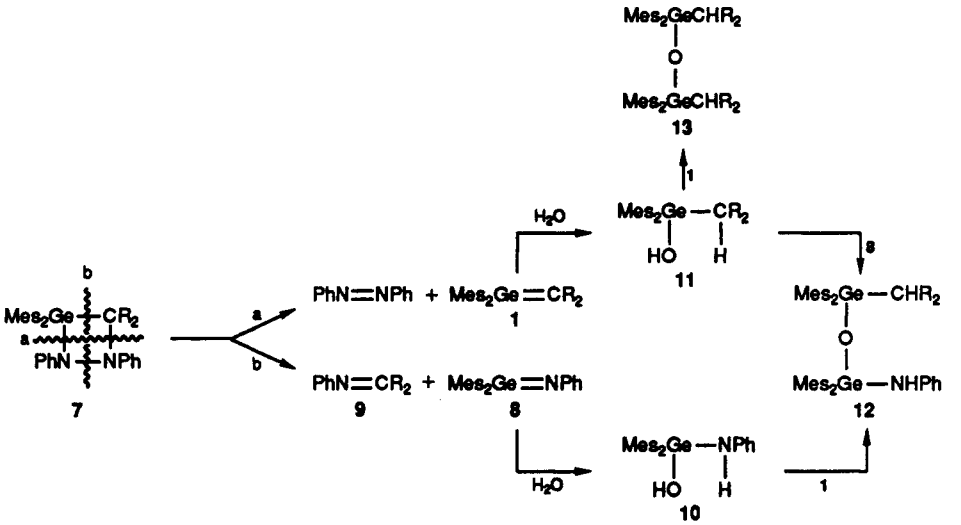
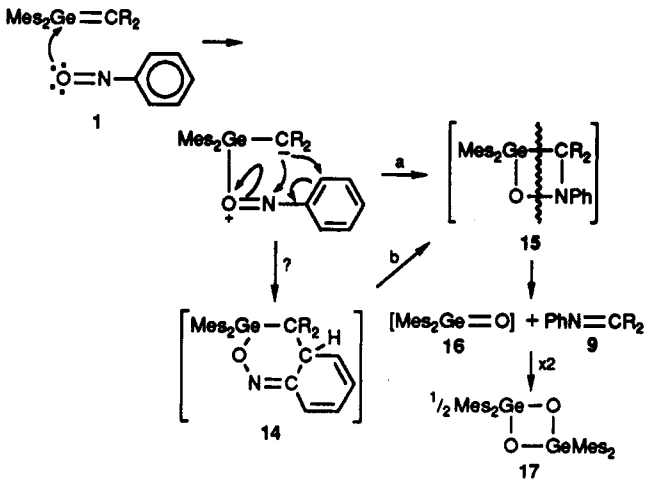
Scheme III



Scheme IV



(q, ^3J(HH) = 7.1 Hz, 1 H, CHN), 3.45 (q, ^3J(HH) = 7.1 Hz, 1 H, CHN), 6.13 (s, 1 H, *CH*Ph), 6.60 (s, 2 H, arom Mes), 6.64 (s, 2 H, arom Mes), 6.58–7.88 (m, 13 H, Ph and CR_2). ^{13}C NMR ($CDCl_3$): δ 15.38, 20.93, 22.57, 24.04 (CH_3CH_2, *o*-Me, *p*-Me), 43.09 (CH_2N), 66.55 (*C*CH), 72.26 (CH), 118.63–128.91 (*m*-C Mes, Ph, C_1–C_8), 135.95–149.32 (ipso Ph, ipso Mes, *o*-C Mes, *p*-C Mes, C_{10}, C_{11}, C_{12}, C_{13}). Mass spectrum (EI, ^{74}Ge; *m/e* (relative intensity)): 609 (M, 1.5), 476 ($Mes_2Ge{=}CR_2$, 34), 311 (Mes_2Ge - 1, 43), 192 (MesGe, 15), 133 (PhCH=NEt, 22), 132 (PhC=NEt, 31), 91 (PhCH + H, 100). Anal. Calcd for $C_{40}H_{41}GeN$: C, 78.97; H, 6.79; N, 2.30. Found: C, 78.72; H, 6.90; N, 2.09.

Reaction of 1 with (Diphenylmethylidene)amine. A solution of (diphenylmethylidene)amine (0.68 g, 3.78 mmol) in Et_2O (6 mL) was added to a solution of germene 1 (1.80 g, 3.78 mmol) in the same solvent (20 mL). After 10 min of stirring, the reaction mixture turned from orange to light yellow. The solvents were then eliminated in vacuo; slow crystallization in pentane allowed the isolation of pure 4: white crystals, 1.67 g (65%); mp 227–228 °C. ^1H NMR (C_6D_6): δ 1.82 (s, 6 H, *p*-Me), 2.00 (s, 12 H, *o*-Me), 4.93 (s, 1 H, CH), 6.23 (s, 4 H, arom Mes), 6.57–8.00 (m, 13 H, Ph and CR_2). ^{13}C NMR ($CDCl_3$): δ 20.83 (*p*-Me), 34.35 (*o*-Me), 47.55 (CH), 119.39 (C_4, C_5), 125.13, 125.54, 125.96 (C_1, C_2, C_3, C_6, C_7, C_8), 127.59, 127.61, 128.73, 128.90, 135.95, 137.74, 141.11, 141.62, 142.76, 145.83 (Ph, arom Mes, C_{10}, C_{11}, C_{12}, C_{13}), 174.57 (C=N). IR (Nujol): ν(C=N) 1625 cm^{-1}. Mass spectrum (EI, 70 eV, ^{74}Ge; *m/e* (relative intensity)): 657 (M, 10), 492 ($Mes_2Ge{-}N{=}CPh_2$, 100); 477 (Mes_2GeCHR_2, 20). Anal. Calcd for $C_{44}H_{41}GeN$: C, 80.51; H, 6.29. Found: C, 80.41; H, 6.35.

Reaction of 1 with Azobenzene. Azobenzene (0.76 g, 4.20 mmol), in solution in benzene (10 mL), was added to a solution of germene 1 (2.0 g, 4.20 mmol) in Et_2O (20 mL) cooled to 0 °C. When the reaction mixture reached room temperature, a red coloration appeared. After 5 h of stirring in refluxing Et_2O, solvents were eliminated in vacuo. Recrystallization in a Et_2O/pentane mixture (20/80) gave 1.61 g (58%) of red crystals of 5, mp 110 °C. ^1H NMR ($CDCl_3$): δ 1.07 (s, 3 H, CH_3), 1.25 (s, 3 H, CH_3), 1.28 (s, 3 H, CH_3), 2.08 (s, 3 H, CH_3), 2.33 (s, 3 H, CH_3), 2.93 (s, 3 H, CH_3), 4.50–4.62 (m, 1 H, HC=CH–), 5.00–5.12 (m, 1 H, HC=CH), 5.30–5.72 (m, 2 H, –HC=CH–), 6.35 (s, 2 H, arom Mes), 6.51 (s, 1 H, arom Mes), 6.62 (s, 1 H, arom Mes), 6.38–8.18 (m, 13 H, Ph and CR_2). ^{13}C NMR ($CDCl_3$): δ 20.83, 21.13, 22.83, 23.24, 23.28, and 25.16 (*o*-Me and *p*-Me), 44.29 (CR_2), 45.74 (*C*H–CR_2), 119.52–150.88 (Ph, arom Mes and CR_2). IR (KBr): ν(C=N) 1593 cm^{-1}. Mass spectrum (EI, 70 eV, ^{74}Ge; *m/e* (relative intensity)): 658 (M, 15), 476 ($Mes_2Ge{=}CR_2$, 90), 403 (Mes_2GeNPh, 10), 255 ($R_2C{=}NPh$, 90), 182 (PhN=NPh, 90). Anal. Calcd for $C_{43}H_{40}N_2Ge$: C, 78.55; H, 6.13; N, 4.26. Found: C, 78.81; H, 6.22; N, 4.33.

Synthesis of 6. A solution of 5 (0.55 g, 0.83 mmol) in Et_2O (10 mL) was left in a small flask at room temperature for 10 days. The initial red solution progressively turned red-brown. After evaporation of Et_2O, recrystallization in pentane afforded brown crystals of 6, in nearly quantitative yield; mp 166–167 °C. ^1H NMR ($CDCl_3$): δ 1.80–2.39 (very broad signal due to slow rotation of *o*-Me and *p*-Me groups), 5.72 (s, 1 H, NH), 6.58–8.05 (m, 21 H, arom Mes, 2 Ph and CR_2). ^{13}C NMR ($CDCl_3$): δ 20.96 (*p*-Me), 24.32 (*o*-Me), 57.24 (CR_2), 115.00–152.01 (arom Mes, Ph, and CR_2). IR (KBr): ν(NH) 3427 cm^{-1}. Mass spectrum (EI, 70 eV, ^{74}Ge; *m/e* (relative intensity)): 658 (M, 2), 254 ($R_2C{-}C_6H_4{-}N$, 49), 105 (PhNN, 100), 91 (PhN, 55), 77 (Ph, 84).

Synthesis and Thermolysis of 7. A solution of 5 (1.25 g, 1.90 mmol) in benzene (15 mL) was heated in a sealed tube at 100 °C for 2 h. Analysis of the reaction mixture by NMR spectroscopy after elimination of C_6H_6 shows the formation, in about 70% yield, of 7, along with unidentified products. Purification of 7 was unsuccessful. ^1H NMR ($CDCl_3$): δ 2.01–2.70 (very broad signal for *o*-Me and *p*-Me, due to their slow rotation), 6.43–6.67 (broad signals, arom Mes), 6.87–8.06 (m, 18 H, Ph, CR_2).

Prolonged heating of 7 in 10 mL of C_6H_6, with 0.3 equiv of water, at 150 °C overnight leads to the disparition of 7. Careful successive recrystallizations in an Et_2O/pentane mixture (10/90) give 13 and then 12. 13: 0.1 g (11%); mp 299–300 °C; identified as the compound directly obtained by reaction of the germene with 0.5 equiv of water.[5] 12: 0.24 g (28%); mp 262–263 °C; ^1H NMR ($CDCl_3$) δ 1.71 (s, 12 H, *p*-Me), 2.24 (s, 12 H, *o*-Me), 2.27 (s, 12 H, *o*-Me), 3.29 (s, 1 H, NH), 4.93 (s, 1 H, CH), 6.17–6.64 (m, 5 H, Ph), 6.64 (s, 4 H, arom Mes), 6.72 (s, 4 H, arom Mes), 6.94 (t, $^3J_{HH}$ = 8.2 Hz, 2 H, CR_2), 7.14 (t, $^3J_{HH}$ = 8.2 Hz, 2 H, CR_2), 7.34 (d, $^3J_{HH}$ = 8.2 Hz, 2 H, CR_2), 7.69 (d, $^3J_{HH}$ = 8.2 Hz, 2 H, CR_2). ^{13}C NMR ($CDCl_3$) δ 21.12 (*p*-Me), 23.47 (*o*-Me), 23.80 (*o*-Me), 46.59 (CH), 116.34–147.70 (arom Mes, Ph and CR_2). IR (KBr): ν(NH) 3399.8 cm^{-1}.

Reaction of 1 with Nitrosobenzene. A solution of nitrosobenzene (0.35 g, 3.30 mmol) in benzene (5 mL) was added to a solution of germene 1 (3.30 mmol) in Et_2O (20 mL) cooled to −78

°C. The reaction mixture turned immediately from orange to dark brown. After the mixture was warmed to room temperature for 2 h, it became progressively yellow. Solvents were eliminated in vacuo, and the crude residue was recrystallized in pentane. The digermadioxetane **17** was the first to crystallize (0.56 g, 52%, white crystals, mp 125–126 °C). ^{1}H NMR (C_6D_6): δ 1.47 (s, 12 H, *p*-Me), 1.98 (s, 24 H, *o*-Me), 6.53 (s, 8 H, arom Mes). Mass spectrum (EI, 70 eV, ^{74}Ge; *m/e* (relative intensity)): 654 (M, 20), 535 (M – Mes, 30), 329 (Mes_2Ge=O + H, 100). Yellow crystals of imine **9**[8] were also obtained, after **17**.

Registry No. **1**, 108946-03-8; **2**, 132774-99-3; **4**, 132775-01-0; **5**, 132775-02-1; **6**, 132775-03-2; **7**, 132775-04-3; **9**, 10183-82-1; **12**, 132775-00-9; **13**, 132775-05-4; **17**, 132775-06-5; PhCH=NEt, 6852-54-6; Ph_2C=NH, 1013-88-3; PhN=NPh, 103-33-3; PhNO, 586-96-9.

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Aromatic and Benzylic C–H Activation. Synthesis and Structural Characterization of Iridium 2-Phenylpyridine and 8-Methylquinoline Complexes

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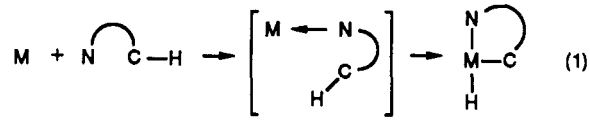
The reaction of 2-phenylpyridine (ppyH) or 8-methylquinoline (mqH) with [*trans*-Ir(CO)(CH_3CN)(PPh_3)$_2$]PF_6 (**1**) at 25 °C gives the four-coordinate complex [Ir(CO)(HL)(PPh_3)$_2$]PF_6 (**2**, HL = ppyH; **3**, HL = mqH), wherein the ligand is N-coordinated. Cyclometalated hydrido complexes [Ir(H)(L)(CO)(PPh_3)$_2$]PF_6 (**4**, L = ppy; **5**, L = mq) can be obtained in low yield by the same reaction at higher temperature. All complexes have been characterized by ^{1}H, ^{31}P, and ^{13}C NMR spectroscopies. The molecular structure of **3** has been determined by X-ray analysis. The complex is monoclinic, space group $C2/c$, with a = 36.973 (7) Å, b = 10.782 (3) Å, c = 27.145 (5) Å, β = 119.682 (13)°, and Z = 8. The iridium atom has a distorted square-planar coordination, with trans P atoms, one CO ligand, and the η^1-bonded mqH. The latter ligand is nearly planar and orthogonal to the coordination plane, with the methyl group in a pseudoaxial position (Ir–C(11) = 3.147 (13 Å).

Introduction

Intramolecular C–H activation by transition metals has been widely investigated,[1–8] yet there is still considerable interest in the study of cyclometalated species,[9–13] particularly with regard to their electrochemical and photophysical properties.[9,11,13]

Many investigations involve platinum group metals (group 8–10) and aromatic N-donor ligands.[14] In all cases, initial N-coordination is believed to precede the cyclometalation (eq 1).



(1)

We have recently reported[15] that 7,8-benzoquinoline (bqH) reacts with [*trans*-Ir(CO)(CH_3CN)(PPh_3)$_2$]PF_6[16] (**1**)

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