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Polarizable stilbazole-based organometallic complexes and polymers *

Juan Burdeniuk and David Milstein

Department of Organic Chemistry, The Weizmann Institute of Science, Rehovot 76100 (Israel)

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Abstract

Oxidative addition reactions of *trans*-4′-bromo-4-stilbazole (**1**) to $Pd(PMe_3)_4$, $Pd(PEt_3)_4$, and $Pd(P^iPr_3)_3$ yield the corresponding Pd^{II} complexes (**5**). The quaternary complexes (**6** and **7**) are obtained by methylation and protonation of **5**. Bromide abstraction from **5** leads to the charged polymers **9**. Comparison of the spectroscopic properties (UV, IR, NMR) of these complexes, as well as those of the gold complex **4**, with those of the parent organic compounds indicates that there is considerable metal participation in the conjugated systems.

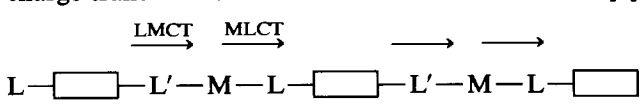
The oscillator strength (f) for the π–π^* transition of the various compounds has been determined. The Pd and Au complexes have considerably higher f values than the parent bromostilbazoles, while palladium complexes exhibit a lower energy π–π^* transition than the latter. The nature of the phosphine ligand in the palladium complex has a minor effect on conjugation.

1. Introduction

Dipolar and polarizable molecules are potential candidates for the preparation of materials that exhibit large macroscopic nonlinearity [1]. Among the organic compounds which show large molecular second harmonic polarizability (β) are conjugated molecules which have an asymmetric charge distribution in the π-system as a result of the presence of donor and acceptor substituents, such as 4,4′-disubstituted stilbenes.

Second harmonic generation with organometallic systems has not been much studied until recently [2].

We are exploring the possibility of generation of extended conjugated networks containing metals in which the metal bridges in an asymmetrical way, so as to promote metal to ligand, as well as ligand to metal, charge transfer with the termini bound to the metal [3].

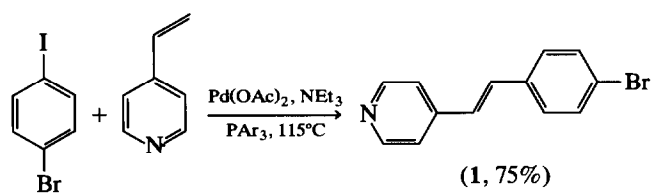


In this work we have prepared such systems in which 4-stilbazole is the bridging unit. We describe here the preparation and spectral properties of stilbazole complexes obtained by oxidative addition of 4-bromo-4′-stilbazole to Pd^0 complexes, and compare them with the parent bromostilbazole and its derivatives. Palladium-containing polymers have been obtained by abstraction of the bromide ligand from the palladium complex. We also describe the complex of gold with 4-bromo-stilbazole. The use of $M(PEt_3)_2(X)$ (M = Pd, Pt; X = Br, I) as donors in donor–acceptor benzene systems has been described before [2f].

2. Results and discussion

2.1. Synthesis of stilbazole ligands

trans-4′-Bromo-4-stilbazole was prepared by a Heck-type reaction [4] of 4-bromoiodobenzene with 4-vinylpyridine (eqn. (1)).



(1)

The reaction is best carried out in neat triethylamine. $P(o\text{-tolyl})_3$ was used although it was later found that PPh_3 is equally effective.

Correspondence to: Professor D. Milstein.

* Dedicated to Professor Gian Paolo Chiusoli in recognition of his important contributions to organometallic chemistry and its applications in organic synthesis.

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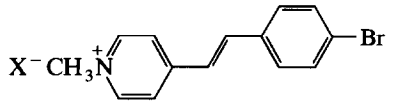
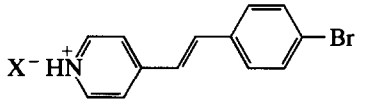
The ^1H NMR spectrum of **1** exhibits a coupling constant of 16 Hz between the olefinic protons, indicating *trans* configuration. Reaction of 4-iodopyridine with 4-bromostyrene was less satisfactory for the preparation of **1**.

In order to increase the dipole moment, the pyridine moiety of **1** was quaternized. Reaction of **1** with methyl iodide and with Me_2SO_4 afforded the *N*-methyl salts **2a** and **2b**, respectively. Anion exchange of **2a** with $AgPF_6$ and $AgBF_4$ yielded the corresponding salts **2c** and **2d**. Protonation of **1** with *d*-camphor sulphonic acid yielded the salt **3**. The chiral acid was employed in order to promote crystallization in a non-centrosymmetric fashion.



(**2a**, X = I;
2b, X = CH_3SO_4;
2c, X = PF_6;
2d, X = BF_4)



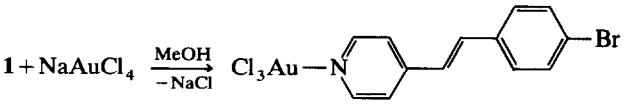
(**3**, X = *d*-camphor sulphonate)

2.2. Synthesis of complexes

2.2.1. Neutral complexes

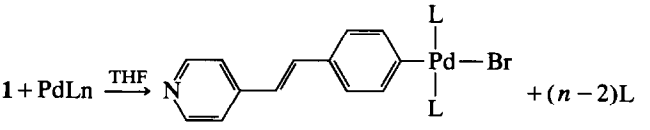
Complexes derived from bromostilbazole can, in principle, be based on coordination to nitrogen or on a σ-carbon bond generated by oxidative addition of a metal to the C–Br bond.

Upon addition of a methanolic solution of $NaAuCl_4$ to solution of **1**, a brick-red precipitate of **4** is immediately formed (eqn. (2)). An analogous reaction with pyridine is well known [5].



(**4**) (2)

Oxidative addition of the C–Br bond of **1** to the Pd^0 trialkylphosphine complexes takes place at room temperature in THF (eqn. (3)).



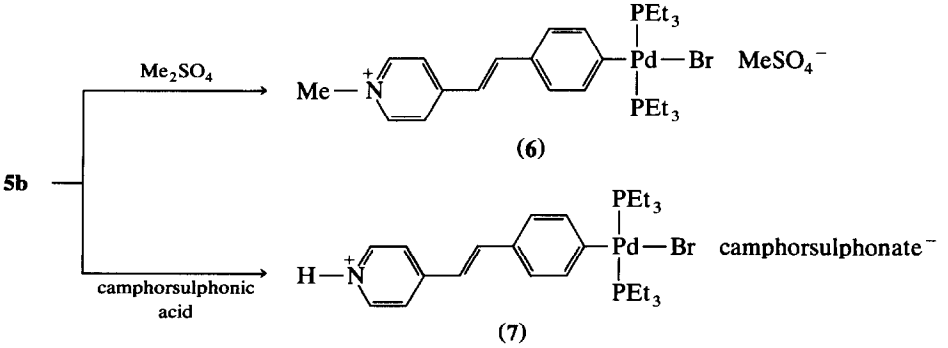
(**5a**, L = PMe_3 ($n = 4$);
5b, L = PEt_3 ($n = 4$);
5c, L = P^iPr_3 ($n = 3$)) (3)

In the case of L = PMe_3, a white precipitate had formed after 2 days' stirring, although most of the product was in solution. After evaporation of the THF the residual solid was crystallized from benzene to give white crystals of **5a** in 90% yield. In the case of **5b** and **5c**, the pure complexes were obtained by evaporation of the THF, pentane washing of the residue and crystallization by slow evaporation of a solution in acetonitrile.

2.2.2. Quaternized complexes

Initially, oxidative addition of the salts **2** and **3** to the Pd^0 trialkylphosphine complexes was attempted, but this gave mixtures, probably because of competing transfer of proton (or alkyl) from the pyridinium compound to Pd^0. A much better route involves quaternization of the neutral Pd^{II} complexes (eqn. (4)).

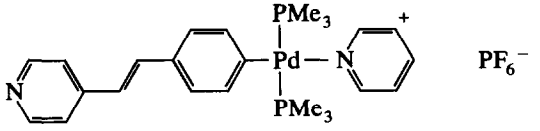
Addition of Me_2SO_4 to a solution of **5b** in THF immediately produces a yellow precipitate of pure **6**. Complex **7** is obtained as an amber powder.



(**6**) (**7**) (4)

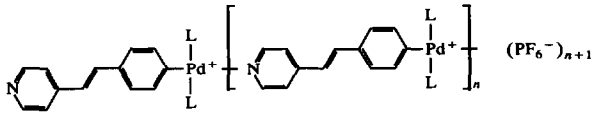
2.2.3. Polymers

Generation of an empty coordination site by bromide abstraction from complexes **5** is expected to lead to polymer formation. Since addition of $AgPF_6$ to an acetone/DMF solution of **5a** led immediately to precipitation of the product together with AgBr, we used acetone/pyridine as a solvent. After filtration to remove AgBr, a solution containing the cationic complex, **8** was obtained, and evaporation of the solvent gave complex **8** as a white powder.



(8)

When heated at 60°C under high vacuum, the coordinated pyridine molecule is removed, yielding a light violet powder of polymer **9**, highly insoluble in organic solvents except pyridine.



(**9a**, L = Me_3P;
9b, L = P^iPr_3)

The ^{31}P NMR spectrum of **9a** in pyridine-d_6 shows a singlet at −22 ppm and a septet for PF_6^- in the expected 2/1 ratio. The ^1H NMR shows a virtual triplet for the methyls of the *trans* phosphines at 1.2 ppm ($J = 3.6$ Hz). The polymer is depolymerized in pyridine to yield the monomeric solvate **8**. We prepared the polymer **9b** in an analogous way to **9a**, thinking that the bulkier phosphine would render it more soluble, but it was also very insoluble in all solvents tried (including DMF and DMSO) except pyridine.

2.3. Spectroscopic properties

2.3.1. Infrared

Increased conjugation in the ground state upon derivatization of **1** is expected to result in a lower bond order for the double bond, with concomitant lowering of the C=C stretching frequency, and this is, indeed, observed (Table 1).

As expected the lowest energy C=C stretching vibration is observed for the organopalladium polymer (**9a**), which has a frequency of 45 cm^{-1} below that for **1**, indicating considerable conjugation.

A large effect on the frequency is also observed upon coordination of gold to nitrogen, a decrease of 41 cm^{-1} compared with that for the parent stilbazole.

TABLE 1. C=C stretching vibration frequencies

Compound	ν(C=C) (cm^{-1}) (Nujol)
1	1650
2a	1640
2b	1646
2c	1643
2d	1645
3	1623
4	1609
5a	1630
5b	1630
5c	1628
6	1611
7	1612
9a	1605

This effect is much larger than that observed upon nitrogen quaternization (compounds **2**, **3**), indicating participation of the metal in the delocalized system.

Oxidative addition of Pd^0 to the C–Br bond of **1** also weakens the C=C bond, but the effect is smaller.

A drop in the C=C stretch is observed also in the quaternized compounds **6**, **7** relative to the uncomplexed salts **2**, **3**. Variation in the size of the phosphine ligands has almost no effect on the C=C stretching frequency.

2.3.2. NMR

No systematic correlation between conjugation and ^1H, ^{31}P NMR was observed.

Upon coordination or quaternization of the aromatic nitrogen, a slight upfield shift of approx. 0.2–0.5 ppm is observed for the hydrogens *ortho* to nitrogen. A systematic study of ^{13}C and ^1H NMR spectra of arylbromobis(triethylphosphine)palladium(II) complexes has been reported [6].

2.3.3. Electronic spectra

The π–π^* charge transfer band is the lowest allowed transition in stilbazole compounds [7]. Table 2

TABLE 2. π–π^* charge transfer transition data

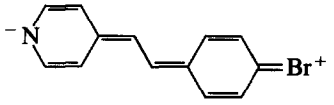
Compound	$\lambda_{\pi-\pi^*}$ (nm)	ϵ	$\Delta E_{\pi-\pi^*}$ (kcal/mol)	f
1	312	33800	91.7	0.51
2a	351	20435	81.7	0.367
2b	354	37820	80.8	0.870
2c	350	14500	81.8	0.368
2d	350	24280	81.8	0.550
3	344	29150	82.2	0.500
4	315	27240	90.9	0.870
5a	333	37340	86.0	0.88
5b	333	42830	86.0	0.89
5c	339	49500	84.5	0.80
6	399	20000	71.7	0.28
7	335	12000	85.4	0.25

lists the wavelength (λ), the extinction coefficient (ϵ) and the calculated energy of this transition for the parent bromostilbazole and its derivatives. We also calculated the oscillator strength, f, for each compound, and these values are also shown. Structures **1*–7*** are valence-bond canonical forms of complexes **1–7** which approximate the excited states obtained upon π–π^* transitions of the corresponding complexes **1–7** [8*]. The transition **1–1*** results in charge separation, whereas upon nitrogen quaternization, no charge separation is required, resulting in a decrease in the energy of the **2–2*** transition. A bathochromic shift of approximately 40 nm is observed in the $\lambda_{\pi-\pi^*}$ for complex **2** relative to **1**, corresponding to an approximately 10 kcal/mol reduction in the transition energy. Some variation as a function of the counter anion is observed, perhaps indicating ion pairing.

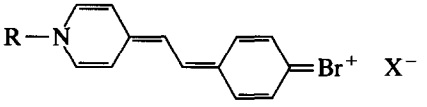
The protonated compound **3** also exhibits a high π–π^* transition at lower energy than **1**, although higher than that for the *N*-methyl derivatives **2**, perhaps because of additional stabilization of the excited state **2*** by hyperconjugation.

Metal coordination to nitrogen in **1** causes only a very slight bathochromic shift, corresponding to ~1 kcal/mol decrease in transition energy. It is instructive to compare this with the very substantial drop in C=C stretching vibration observed in the IR spectrum of **4** relative to that for **1** (see above), indicating a significant increase in ground state delocalization upon Au coordination. It is likely that metal coordination stabilizes both the ground and excited states. In addition, the **4–4*** transition results in charge separation.

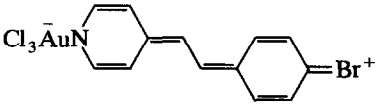
Upon oxidative addition, the palladium moiety σ-bonded to the stilbazole causes a bathochromic shift of the π–π^* transition, indicating participation of the metal (as an electron donor) in the conjugated system (structures **5*–7***). It is noteworthy that a somewhat lower energy transition is observed for L = P^iPr_3 than for L = PMe_3 or PEt_3. This seems surprising, because the desirable coplanarity between the stilbazole ligand and the PdL_2Br group, important for conjugation, would be expected to be more difficult to achieve with L = P^iPr_3, as a result of steric repulsion involving the *ortho* hydrogens. We suggest that steric hindrance facilitates formation of a trigonal planar, Y-shaped complex by dissociation of bromide. Polar solvents, such as methanol in which the UV measurements were carried out, would facilitate the dissociation. The Y-shaped complex would have a lower steric barrier to coplanarity than the square planar complexes of the smaller phosphines.



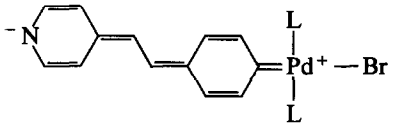
(**1***)



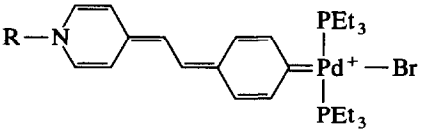
(**2***, R = Me;
3*, R = H)



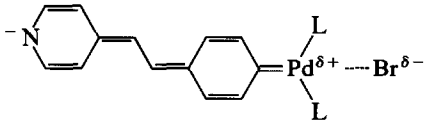
(**4***)



(**5a***, L = PMe_3;
5b*, L = PEt_3)



(**6***, R = Me;
7*, R = H)



(**5c***, L = P^iPr_3)

2.4. *Oscillator strength*

The quadratic hyperpolarizability β, which is an important factor in second harmonic generation (SHG), is composed of two parts [1a,9]:

$$\beta = \beta_{add} + \beta_{CT}$$

β_{add} takes account of all the transitions except that corresponding to intramolecular charge transfer, and is well described by the sum of the effects of individual substituents. The contribution of the intramolecular charge transfer is that of a two level system formed by

* Reference number with asterisk indicates a note in the list of references.

the ground and excited states. The value of β_{CT} is expressed [9] as

$$\beta_{CT} \sim \lambda_{max}^3 \cdot f \cdot \Delta\mu$$

where f is the oscillator strength, $\Delta\mu$ is the difference between the excited and ground states, and λ_{max} is the wavelength of the charge transfer transition. The value of f can be approximated as

$$f = 4.32 \times 10^{-9} \cdot \epsilon_{max} \cdot \Delta\nu_{1/2}$$

$\Delta\nu_{1/2}$ is the absorption band width at half height, and f then expresses the area under the UV absorption band. The f values for the various organic and organometallic compounds are given in Table 2. Since f is directly proportional to β_{CT}, high f values are desirable for SHG.

Examination of Table 2 reveals that the highest f values are exhibited by the gold complex **4** and by the palladium complexes **5a–5c**, all considerably higher than those exhibited by the bromostilbazole **1** and by its salts **2–3**. The similar values of **2a–2c** indicate that the phosphine size has only a minor effect. Complexes **5** have an advantage over **4** in that they exhibit a lower energy π–π^* transition, beneficial for β_{CT}.

A considerable drop in the oscillator strength is observed on going to the quaternized complexes **6** and **7**. It is reasonable to assume that complexes **5a–5c** have a larger dipole moment in the excited state than do **6** and **7**, because of charge separation in the conjugated system (compare structures **5***, **6***, **7***). Moreover, the charged **6** and **7** are expected to have a larger ground state dipole moment than complexes **5**. As a result, a larger difference in the dipole moment between the ground and excited states ($\Delta\mu$) is expected for complexes **5** than for **6**, **7** (Fig. 1.

2.5. Kurtz powder test

The compounds reported in this work were submitted for the Kurtz [11] powder test for valuation of SHG. However, values lower or comparable with that of urea were obtained, perhaps as a result of centrosymmetric crystallization.

3. Experimental details

3.1. General

Syntheses of complexes were carried out under nitrogen by use of a glove box and Schlenk techniques. Benzene, toluene and THF were purified by refluxing over and distillation from sodium benzophenone ketyl under nitrogen. All solvents were degassed prior to use and were stored over activated 4 Å molecular sieves. Phosphines were used as received (Aldrich). 4-Vinylpyridine (Aldrich) was distilled under vacuum prior to use.

NMR measurements were performed on Bruker WH-270, and Bruker 400 AMX spectrometers at 20°C. The chemical shifts are reported in ppm downfield from an external reference: TMS for ^{1}H NMR and 85% orthophosphoric acid in D_2O for ^{31}P NMR.

Infrared spectra were recorded with a Nicolet 510-FTIR spectrometer and are reported in cm^{-1}. All samples were prepared on NaCl discs as films or in Nujol. Samples of (potentially) air-sensitive compounds were prepared in a glove box and taken out in plastic bags under nitrogen. The measurements were carried out under nitrogen flow.

UV measurements were performed with a Hewlett-Packard 8450 diode-array spectrometer; the wavelengths are reported in nm. The samples were prepared in a glove box and the UV quartz cells were sealed prior to taking them out for measurements.

3.2. Synthetic procedures

3.2.1. Stilbazole ligands.

3.2.1.1. trans-4'-Bromo-4-stilbazole (1). In a Fischer-Porter pressure bottle, a mixture of 1-bromo-4-iodobenzene (5.65 g, 20 mmol), 10 ml of triethylamine, 4-vinylpyridine (2.63 g, 25 mmol), tri-*o*-tolylphosphine (0.122 g, 0.4 mmol), and palladium acetate (45 mg, 0.2 mmol) under nitrogen was stirred at 115°C for 48 h. Formation of a new product was observed by TLC and the mixture was worked up by extraction with chloroform and water. The salts dissolved in the water phase, and the chloroform fraction was evaporated and the residue flash chromatographed on a silica column to yield the product in 75–80% yield. Similar results were obtained when triphenylphosphine was used instead of the *o*-tolyl phosphine.

IR (film): 3071w, 3021w, 1650m, 1590vs, 1546m, 1491m, 1414s, 1073m, 1007m, 973vs, 869w, 825vs. ^{1}H NMR ($CDCl_3$): 8.56 (*d*, $J = 5.9$ Hz, 2H); 7.51 (d, $J = 8.47$ Hz, 2H); 7.40 (d, $J = 8.47$, 2H); 7.32 (d, $J = 5.9$ Hz, 2H); 7.20 (d, $J = 16$ Hz, 1H); 7.00 (d, $J = 16$ Hz, 1H). ^{13}C NMR ($CDCl_3$): 151.1 (s), 145.0 (s), 136.7 (s), 132.7 (s), 132.4 (s), 129.6 (s), 127.9 (s), 122.7 (s), 121.8 (s). UV (MeOH): 228 (22 750), 312 (57 600).

3.2.1.2. trans-4'-Bromo-4-stilbazole methiodide (2a). To a stirred solution of stilbazole **1** (200 mg, 0.77 mmol) in 6 ml of THF, a solution of methyl iodide (113 mg, 0.8 mmol) in 2 ml of THF was added dropwise. The mixture was protected from light with aluminium foil and stirred at room temperature for 2 h. A yellow salt separated and was filtered off. IR (film): 3026w,

1640m, 1617vs, 1518s, 1471m, 1326m, 1300w, 1186s, 1069m, 988s, 836s. ^{1}H NMR (acetone-d_6): 9.00 (d, J = 6.6 Hz, 2H); 8.36 (d, J = 6.6 Hz, 2H); 8.06 (d, J = 16 Hz, 1H); 7.62 (d, J = 16 Hz, 1H); 7.73 (d, J = 8.5 Hz, 2H); 7.65 (d, J = 8.5 Hz, 2H); 4.53 (s, 3H). UV (MeOH): 226 (19300), 316 (29480), 325 (27805), 351 (20435).

3.2.1.3. N-methyl-trans-4'-bromo-4-stilbazolium methylsulphate (2b). To a well-stirred solution of stilbazole **1** (200 mg, 0.77 mmol) in 6 ml of THF, a solution of dimethylsulphate (110 mg, 0.88 mmol) in 2 ml of THF was added dropwise. A light yellow precipitate separated and was filtered off, washed with a little THF, and analyzed. The product was partially soluble in THF and more of it was precipitated from the mother liquor by addition of pentane.

IR (film): 3056w, 2942w, 1646m, 1620vs, 1522m, 1475m, 1248vs, 1227vs, 1067m, 1015s, 845s, 736s. ^{1}H NMR (D_2O): 8.41 (d, J = 6.2 Hz, 2H); 7.66 (d, J = 6.2 Hz, 2H); 7.30 (m, 5H); 6.88 (d, J = 16 Hz, 1H); 4.21 (s, 3H); 3.73 (s, 3H). UV (MeOH): 243 (13580), 354 (37820).

3.2.1.4. trans-4'-Bromo-4-stilbazole d-camphorsulphonic acid salt (3). A solution of stilbazole **1** (200 mg, 0.77 mmol) in 6 ml of THF was mixed with a THF solution of *d*-camphor sulphonic acid (178 mg, 0.77 mmol). The white precipitate formed was filtered off and analyzed.

IR (film): 3072w, 2952w, 1736m, 1623s, 1505m, 1160s, 1032s, 846w. ^{1}H NMR (acetonitrile-d_3): 8.69 (d, J = 6.7 Hz, 2H); 8.00 (d, J = 6.7 Hz, 2H); 7.67 (d, J = 16 Hz, 1H); 7.6 (br, 5H); 7.37 (d, J = 16 Hz, 1H); 3.14 (d, J = 11 Hz, 1H); 2.70 (d, J = 11 Hz, 1H); 2.6 (m, 2H); 2.3 (m, 1H); 2.12 (s, 2H); 2.03 (m, 2H); 1.07 (s, 3H); 0.81 (s, 3H). UV (MeOH): Varies with concentration, but two main absorptions were observed: λ_I from 228 to 238 nm and λ_{II} from 297 to 344 nm.

3.2.1.5. N-methyl-trans-4'-bromo-4-stilbazolium hexafluorophosphate (2c). To a solution of stilbazole **2c** (iodide salt) (150 mg, 0.373 mmol) in 7 ml of a 2:1 acetone/methanol mixture, a suspension of silver hexafluorophosphate (95 mg, 0.373 mmol) in 1 ml acetone was added dropwise with stirring. The yellow precipitate of AgI was filtered off and the colorless solution was evaporated under vacuum. The white powder obtained was washed with THF and pentane and dried under high vacuum.

IR (Nujol): 1724w, 1622m, 1544s, 1378s, 825m. ^{1}H NMR (acetone-d_6): 8.94 (d, J = 6.7 Hz, 2H); 8.32 (d, J = 6.7 Hz, 2H); 8.00 (d, J = 16 Hz, 1H); 7.75 (d, J = 8 Hz, 2H); 7.67 (d, J = 8.6 Hz, 2H); 7.60 (d, J = 16 Hz, 1H); 4.52 (s, 3H). ^{31}P NMR (acetone): −142.0 (sept, J(P–F) = 709.9 Hz, 1P). UV (MeOH): 240 (7250), 350 (14500).

3.2.1.6. N-methyl-trans-4'-bromo-4-stilbazolium tetrafluoroborate (2d) The procedure was similar to that used for **2c** but starting with $AgBF_4$.

IR (Nujol): 2900br, 1645m, 1620m, 1519w, 1547vs, 1371vs, 1187m, 1050s, 835m. ^{1}H NMR (acetone-d_6): 8.90 (d, J = 6.5 Hz, 2H); 8.28 (d, J = 6.5 Hz, 2H); 7.98 (d, J = 16 Hz, 1H); 7.74 (d, J = 8 Hz, 2H); 7.65 (d, J = 8.5 Hz, 2H); 7.59 (d, J = 16 Hz, 1H); 4.50 (s, 3H). UV (MeOH): 242 (12560), 350 (24280).

3.2.2. Complexes

3.2.2.1. trans-4'-Bromo-4-stilbazole trichloroauric complex (4). This procedure was similar to that used for pyridine and sodium tetrachloroaurate [5].

A solution of dry $NaAuCl_4$ (140 mg, 0.384 mmol) in 3 ml of methanol was added to a stirred solution of stilbazole **1** (100 mg, 0.384 mmol) in 4 ml of methanol. A red-brick precipitate was immediately formed and was washed with methanol and pentane, then dried under high vacuum.

IR (film): 3449br, 3107w, 1609s, 1489m, 1440s, 1405m, 1330m, 1200s, 1068s, 1010m, 969m, 880w, 828s. ^{1}H NMR (acetone-d_6): 9.00 (d, J = 6 Hz, 2H); 8.39 (d, J = 6.3 Hz, 2H); 8.05 (d, J = 16 Hz, 1H); 7.77 (d, J = 8.6 Hz, 2H); 7.71 (d, J = 3.4 Hz, 2H); 7.68 (d, J = 16 Hz, 1H).

3.2.2.2. trans-4-Stilbazole-4'-[trans-bromobis(trimethylphosphine)palladium] (5a). To a solution of stilbazole **1** in 6 ml of THF (200 mg, 0.77 mmol) was added dropwise a solution of $Pd[PMe_3]_4$ (328 mg, 0.8 mmol) in 4 ml of THF. The reaction was monitored by TLC until completion. The product separated from the THF solution and was filtered off and washed with pentane to remove unchanged $Pd[PMe_3]_4$. The solution was then evaporated, and the residue washed with pentane and recrystallized from benzene. White crystals were obtained (70% yield).

IR (film): 2965w, 2924w, 2905w, 1630w, 1604vs, 1573vs, 1499w, 1479w, 1430w, 1418w, 1097w, 1056m, 1023m, 1013m, 947vs. ^{1}H NMR (acetonitrile-d_3): 8.49 (d, J = 6.2 Hz, 2H); 7.41 (d, J = 6.2 Hz, 2H); 7.35–7.26 (m, 5H); 7.05 (d, J = 16 Hz, 1H); 1.16 (virt t, J = 3.6 Hz, 18H). ^{31}P NMR (THF): −17.8 (s, 2P). UV (MeOH): 333 (37340).

3.2.2.3. trans-4-Stilbazole-4'-[trans-bromobis(triethylphosphine)palladium] (5b). The synthetic procedure was similar to that described for **5a**. However, this

complex is more soluble in THF, and no precipitate was observed during the reaction.

IR (film): 1629m, 1590m, 1573s, 1460s, 1377vs, 880m, 980w, 665w. ^{1}H NMR ($CDCl_3$): 8.54 (d, J = 6.1 Hz, 2H); 7.34 (d, J = 6.1 Hz, 2H); 7.30–7.20 (m, 12H); 6.96 (d, J = 16 Hz, 1H); 1.6 (m, 12H); 1.09 (dxt, J(H–H) = 8, J(P–H) = 14 Hz, 36H). ^{31}P NMR (THF): 13.05 (s, 2P). UV (MeOH): 333 (42 830).

3.2.2.4. trans-4-Stilbazole-4'-[trans-bromobis(triisopropylphosphine)palladium] (5c). The procedure was analogous to that described for **5a**.

IR (film): 1628m, 1593m, 1572s, 1459vs, 1377vs, 1250w, 1040w, 980w, 890m, 720m. ^{1}H NMR ($CDCl_3$): 8.55 (d, br, 2H); 7.47 (d, J = 8 Hz, 2H); 7.33 (d, J = 5 Hz, 2H); 7.18 (d, J = 16 Hz, 1H); 7.12 (d, J = 8 Hz, 2H); 6.90 (d, J = 16 Hz, 1H); 2.38 (m, 6H); 1.24 (dxd, J(H–H) = 8, J(P–H) = 14 Hz, 36H). ^{31}P NMR (THF): 31.3 (s, 2P). UV (MeOH): 277 (35 800), 339 (49 500).

3.2.2.5. N-Methyl-trans-4-stilbazolium-4'-[trans-bromobis(triethylphosphine)palladium] methylsulphate (6). To a well-stirred solution of the stilbazole palladium complex **5b** (400 mg, 0.66 mmol) in 6 ml of THF was added dropwise a solution of dimethyl sulphate (83 mg, 0.66 mmol) in 1 ml of THF. After 30 min a yellow orange precipitate was obtained, and this was filtered off and vacuum dried. (yield ≈ 85%).

IR (film): 1644vw, 1611m, 1566w, 1463s, 1377s, 1164m, 1050w, 980w, 740s. ^{1}H NMR ($CDCl_3$): 8.83 (d, J = 6.7 Hz, 2H); 7.92 (d, J = 6.7 Hz, 2H); 7.62 (d, J = 16 Hz, 1H); 7.41 (d, J = 8.0 Hz, 2H); 7.28 (d, J = 8.0 Hz, 2H); 7.06 (d, J = 16 Hz, 1H); 4.43 (s, 3H); 3.76 (s, 3H); 1.09 (dxt, J(H–H) = 8, J(P–H) = 14 Hz, 18H); 1.61 (m, 12H). ^{31}P NMR (THF): 15.08 (s, 2P). UV (MeOH): 260 (30 440), 399 (20 000).

3.2.2.6. trans-4-Stilbazolium-4'-[trans-bromobis(triethylphosphine)palladium. Camphor sulphonate (7). To a solution of the stilbazole palladium complex **5b** (400 mg, 0.66 mmol), in 6 ml of THF was added dropwise a solution of *d*-camphorsulphonic acid (153 mg, 0.66 mmol) in 2 ml of THF. An immediate change in color from yellow to amber was observed. The THF was evaporated and the residual solid washed with pentane and vacuum dried (yield ≈ 90%).

IR (film): 1740m, 1612m, 1571m, 1462s, 1377s, 1198w, 1033s, 790m, 726m. ^{1}H NMR ($CDCl_3$): 8.73 (d, J = 6.6 Hz, 2H); 7.83 (d, J = 6.6 Hz, 2H); 7.54 (d, J = 16 Hz, 1H); 7.33 (d, J = 7.8 Hz, 2H); 7.21 (d, J = 7.8 Hz, 2H); 7.05 (d, J = 16 Hz, 1H); 3.34 (d, J = 14.5 Hz, 1H); 2.88 (d, J = 14.5 Hz, 1H); 2.66 (m, 1H); 2.22 (m, 1H); 2.0–1.7 (m, 5H); 1.53 (m, 12H); 1.05 (dxt + s, 21H); 0.79 (s, 3H). ^{31}P NMR (THF): 14.1 (s, 2P). UV (MeOH): 335 (12 000).

3.2.2.7. Stilbazole palladium polymer (9a). The stilbazole palladium complex **5a** (200 mg, 0.385 mmol) was dissolved in a solvent mixture acetone/pyridine (1/1). Silver hexafluorophosphate (98 mg, 0.385 mmol) was suspended in acetone, and this suspension and the solution of **5a** were cooled for 1.5 h at −40°C. The cold $AgPF_6$ suspension was added dropwise to the cool and well-stirred solution of the Pd^{II} complex with exclusion of light by use of aluminum foil. Immediate precipitation of AgBr was observed. The product was worked up either by filtration or by centrifugation. In the case of centrifugation the tubes were protected from light and sealed to protect them from air. The precipitate was extracted twice with a 1/1 pyridine/acetone mixture. The solvent was removed from the combined mother liquor and washings under vacuum to yield as a white powder, the pyridine complex **8**, which was washed with toluene and pentane, then dried under high vacuum. Heating at 60°C under high vacuum resulted in a gradual polymerization. The heating was continued until the weight remained constant (3 days), yielding the polymer as an amber solid (≈ 90% yield).

IR (film): 2963w, 2911w, 2859vw, 1717w, 1606s, 1573s, 1480m, 1415w, 1278w, 1117w, 1061m, 945s, 840s, 740s. ^{31}P NMR (pyridine): −22.2 (s, 2P); −146 (sept, J(P–F) = 709.5 Hz, 1P). ^{1}H NMR (pyridine-d_5): Peaks of solvent superimpose the ones of stilbazole unit. 1.12 (virt t, J = 3.6 Hz, 2xPMe_3 *trans*). Elemental analysis: Found: C, 38.69; H, 4.21; N, 1.93. $[C_{19}H_{28}NP_3F_6Pd]_n$ calc.: C, 39.08; H, 4.80; N, 2.40%.

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