Synthesis and Reactivity toward Alkynes of 2-Formyl- and 2-Acetylarylpalladium(II) (Aryl = Phenyl and 5-Nitrophenyl) Complexes. Formation of Indenols and Indenones

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The imine $C_6H_4(CH{=}N^nBu)(NO_2)$-4 reacts with palladium acetate to give the cyclopalladated $[Pd_2\{\kappa^2\text{-}C,N\text{-}C_6H_3(CH{=}N^nBu)\text{-}2\text{-}(NO_2)\text{-}5\}_2(\mu^2\text{-}OAc)_2]$ (**1**). This complex is hydrolyzed in the presence of bromide and 2,2′-bipyridine (bpy) or PPh_3, affording the *ortho*-formylaryl complexes $[Pd\{C_6H_3(CHO)\text{-}2\text{-}(NO_2)\text{-}5\}Br(bpy)]$ (**2**) or *trans*-$[Pd\{C_6H_3(CHO)\text{-}2\text{-}(NO_2)\text{-}5\}Br(PPh_3)_2]$ (**3**), respectively. Complex **2** reacts with pyridine (py) or PPh_3 in the presence of Tl(TfO) (TfO = CF_3SO_3), giving the cationic species $[Pd\{C_6H_3(CHO)\text{-}2\text{-}(NO_2)\text{-}5\}(py)(bpy)](TfO)$ (**4**) or $[Pd\{C_6H_3(CHO)\text{-}2\text{-}(NO_2)\text{-}5\}(bpy)(PPh_3)](TfO)$ (**5**), respectively. Similarly, the compounds $[Pd\{C_6H_4C(O)X\text{-}2\}Br(bpy)]$ [X = H (**6**), Me (**7**)] react with py and Tl(TfO) to give $[Pd\{C_6H_4C(O)X\text{-}2\}(py)(bpy)](TfO)$ [X = H (**8**), Me (**9**)]. The reactions of the neutral complex **2** or **6** with Tl(TfO) and the alkynes PhC≡CPh, EtC≡CEt, or MeC≡CPh at room temperature result in the formation of 2,3-R,R′-5-X-1*H*-inden-1-ol [X = NO_2, R = R′ = Ph (**10a**), Et (**10b**), R = Ph, R′ = Me (**10c**); X = H, R = R′ = Ph (**11a**), Et (**11b**), R = Ph, R′ = Me (**11c**)]. By contrast, the reactions of the cationic complex **4** or **8** with the same alkynes at 90 °C for a long period of time give 2,3-R,R′-5-X-inden-1-ones [X = NO_2, R = R′ = Ph (**12a**), Et (**12b**), R = Ph, R′ = Me (**12c**); X = H, R = R′ = Ph (**13a**), Et (**13b**), R = Ph, R′ = Me (**13c**)]. This contrasting behavior is discussed and compared with the result of the reaction of the 2-acetylarylpalladium(II) complex **7** with the same alkynes which renders 2,3-R,R′-1-methyl-1*H*-inden-1-ol [R = R′ = Ph (**14a**), Et (**14b**), R = Ph, R′ = Me (**14c**)]. Complex **9** reacts with MeC≡CPh to give **14c**.

Introduction

Indenones have been used as fungicides, estrogen-binding receptors, and fermentation activators, and they are useful intermediates in the synthesis of some natural products such as steroids or gibberellins.[1,2] They can be prepared following classical organic synthetic methods[3] or by metal-mediated reactions using alkynes and carbonyl complexes of rhodium,[4] nickel,[5] or iron.[6,7] In these cases the indenone carbonyl comes from a coordinated CO. The metal-catalyzed synthesis of indenones has been achieved from *o*-alkynyl-substituted α-diazoacetophenone in the presence of rhodium(II) carboxylates,[8,9] by palladium-catalyzed reactions of alkynes with *o*-diiodobenzenes, Zn, and CO,[5] by reaction of alkynes with 2-bromobenzaldehyde, 2-iodobenzaldehyde,[1,10] or 2-iodobenzonitrile[11] in the presence of a palladium catalyst, and by reacting aroyl chlorides with internal alkynes using $[RhCl(cod)]_2$ as catalyst.[12]

Indenols are intermediates in the synthesis of organic compounds such as indenyl chrysanthemates, which have insecticidal properties.[13,14] Other indenols have shown analgesic and myorelaxation activity.[15] These substances can be prepared from *o*-manganated aryl

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ketones or benzaldehydes and alkynes.[16−19] More recently, a palladium-catalyzed synthesis of indenols has been reported.[20−22]

We have studied the reactivity of 6-formyl-2,3,4-trimethoxyphenyl-, 2-formyl-3,4,5-trimethoxyphenyl-, and 6-acetyl-2,3,4-trimethoxyphenylpalladium complexes with alkynes, and depending on the reaction conditions, the charge of the complex, the nature of the ligands coordinated to the palladium atom, and the alkyne substituents, we have obtained indenols, indenones, benzofulvenes, and spirocyclic compounds,[23−28] after the insertion of the alkynes into the C−Pd bond. Indenols were preferentially formed when starting from cationic *ortho*-formylaryl complexes in the presence of moisture or added water. Neutral or anionic complexes gave mixtures of indenol and indenones depending on the degree of moisture present in the solvent. Indenones were formed under anhydrous conditions or starting from an anionic complex.[23] Cationic *ortho*-acetylaryl complexes always gave indenols,[23] while a neutral complex led to benzofulvenes or spirocyclic compounds depending on whether an aryl group was present in the alkyne.[24] In view of these results, we decided to carry out a study with neutral and cationic *ortho*-formyl- and *ortho*-acetylarylpalladium(II) complexes not having electron-releasing methoxy groups in the arene ring as those previously studied. We have recently reported the synthesis of the 2-formyl- and 2-acetylphenyl complexes [Pd{$C_6H_4C(O)X$-2}Br(bpy)] [X = H, Me] through oxidative addition reactions and their reactivity toward PhC≡CPh and EtC≡CEt.[27] We extend here this study (i) to the reactivity of the last complexes toward the unsymmetrical alkyne MeC≡CPh to know the regioselectivity of the insertion reactions, (ii) to the synthesis of the first 2-formyl-5-nitrophenylpalladium(II) derivatives, (iii) to the synthesis of new cationic 2-formyl- and 2-acetylphenyl complexes, and (iv) to the reactivity of these neutral and cationic complexes toward PhC≡CPh, EtC≡CEt, and MeC≡CPh in order to know the influence of the charge of the complex in such insertion reactions.

The syntheses of the desired 2-formyl-5-nitrophenylpalladium(II) complexes have not been an easy task because neither the lithium or Grignard reagents nor the haloarenes were available to prepare them through transmetalation or oxidative addition reactions, respectively. We report the first 2-formyl-5-nitrophenyl complexes through a cyclometalation process followed by a hydrolytic reaction. We have previously applied this method for the first time to prepare dipalladated terephthaldehyde complexes.[29]

Results

Synthesis and Characterization of Complexes. We have reported the synthesis of nitroaryl,[30] acetylaryl,[26,31] and formylaryl[26,32−34] palladium complexes using the corresponding mercury derivatives as transmetalating agents. The mercurials were usually prepared by direct mercuration of the corresponding arenes or by decarboxylation of the corresponding carboxylate mercury salts. We have unsuccessfully attempted to mercurate *para*-nitrobenzaldehyde to prepare 2-formyl-5-nitrophenyl mercury. The presence of the two deactivating groups not only renders the mercuration difficult but also gives rise to a mixture of the two possible isomers that we could not separate. We have succeeded in the synthesis of 2-formyl-5-nitrophenylpalladium(II) complexes through a cyclometalation process followed by a hydrolytic reaction. We have previously applied this method for the first time to prepare dipalladated terephthaldehyde complexes.[29] Thus, the imine C_6H_4-(CH=NBu)(NO_2)-4 is palladated by $Pd(OAc)_2$ to give [$Pd_2\{\kappa^2$-C,N-C_6H_3(CH=N^{n}Bu)-2-(NO_2)-5$\}_2(\mu^2$-$OAc)_2$] (**1**) with a 83% yield (Scheme 1). When this compound is treated with 2,2′-bipyridine (bpy) and an excess of NaBr in a 5:2 Me_2CO/H_2O mixture, in the presence of acetic acid, the compound [Pd{C_6H_3(CHO)-2-(NO_2)-5}Br(bpy)] (**2**) is formed and can be isolated with a 70% yield. In a similar manner, using PPh_3 instead of bpy, *trans*-[Pd{C_6H_3(CHO)-2-(NO_2)-5}Br$(PPh_3)_2$] (**3**) is isolated in 60% yield. The same method has been used by us for the synthesis of the only known examples of dipalladated terephthaldehyde derivatives.[29] To the best of our knowledge, these are the first organotransition metal compounds having this aryl group as a ligand. By reaction of **2** with Tl(TfO) (TfO = CF_3SO_3) in the presence of pyridine or PPh_3 the cationic derivatives [Pd{C_6H_3(CHO)-2-(NO_2)-5}(py)(bpy)](TfO) (**4**) and [Pd{C_6H_3(CHO)-2-(NO_2)-5}(bpy)(PPh_3)](TfO) (**5**) can be isolated (Scheme 1).

We have also prepared complexes analogous to **4** but without the nitro group from the previously described complexes[27] [Pd{C_6H_4CHO-2}Br(bpy)] (**6**) and [Pd{$C_6H_4C(O)$Me-2}Br(bpy)] (**7**). Thus, they react with Tl-

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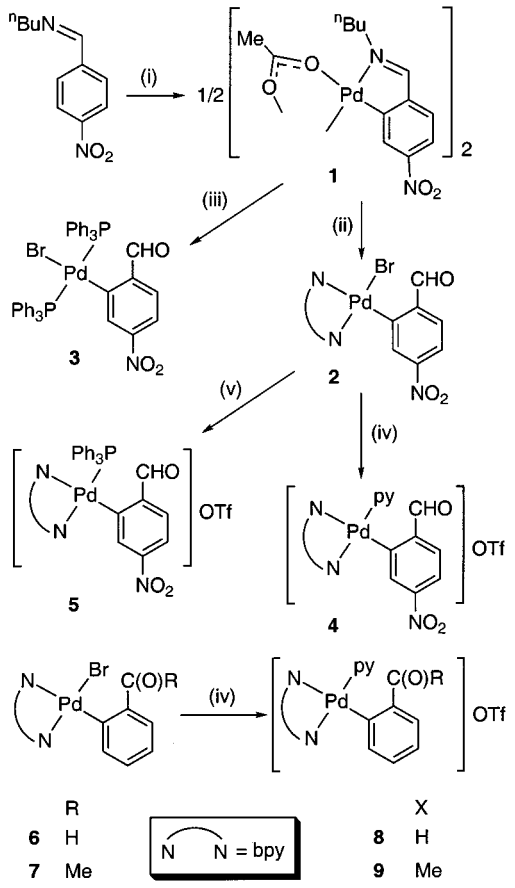
Scheme 1



(TfO) and pyridine to give [Pd{C_6H_4CHO-2}(py)(bpy)](TfO) (**8**) and [Pd{C_6H_4C(O)Me-2}(py)(bpy)](TfO) (**9**), respectively.

The new compounds **2**−**5** and **8** exhibit in their IR spectra a band attributable to the ν(C═O) mode of the formyl groups (1680−1695 cm^{-1}) in the same region as those found in other 2-formylarylpalladium(II) complexes.[26,27,32−34] Similarly, complex **9** shows an absorption corresponding to the ν(C═O) mode of the acetyl group (at 1658 cm^{-1}).[26,27,31]

The ^{1}H NMR and ^{13}C NMR resonances corresponding to the formyl group of the nitroaryl derivatives appear around 11 and 195 ppm, respectively, for complexes containing bpy as the sole neutral ligand [**2** (11.06, 195.26 ppm) and **4** (10.99, 195.18 ppm)], while those having one or two PPh_3 ligands show these resonances at lower chemical shift values [**3** (10.19/193.55 ppm) and **5** (9.97/193.10 ppm)] probably due to ring current effects of the PPh_3 aryl groups. As expected, complex **8** shows these resonances at lower chemical shift values [10.36/194.8 ppm] than those in the nitro-substituted aryl complex **4** (10.99, 195.18 ppm). The ^{31}P NMR spectra of **3** and **5** show the presence of a singlet in accord with their proposed structures (Scheme 1).

Reactions of Complexes with Alkynes. These reactions were carried out without precautions against the presence of oxygen or moisture. The reaction of the

Scheme 2

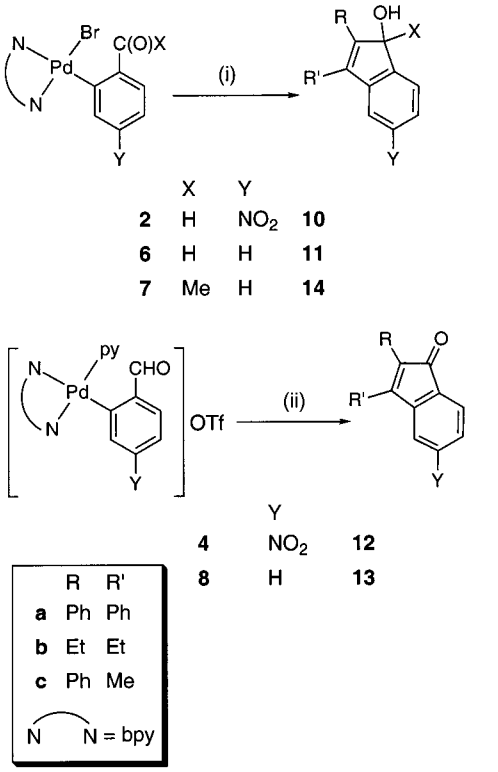
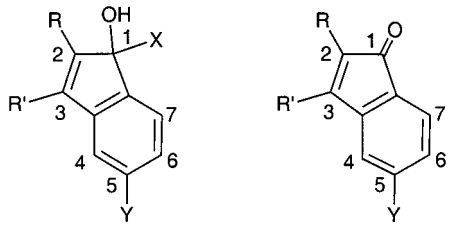


Chart 1



neutral complex **2** with Tl(TfO) and the alkyne RC≡CR′ at room temperature resulted in the precipitation of a mixture of TlBr and [$Pd_2(\mu$-OH)$_2$(bpy)$_2$](TfO)$_2$[23,35] and the formation of the indenol **10a** (R = R′ = Ph; 67%), **10b** (R = R′ = Et; 64%), or **10c** (R = Ph, R′ = Me; 61%) (Scheme 2). Similarly, the neutral complex **6** reacts with the same alkynes to give the indenols **11a** (R = R′ = Ph; 52%), **11b** (R = R′ = Et; 57%), or **11c** (R = Ph, R′ = Me; 53%) along with small amounts of the indenones **13a**, **13b**, and **13c** in 8, 6, and 15% yields, respectively, which were separated using preparative TLC. In the case of PhC≡CMe only the regioisomers **10c** and **11c** having the Me substituent at the 3 position were obtained (see Scheme 2 and Chart 1). In the analogous reactions with **2**, no indenones were detected. By contrast, the reactions of the cationic complex **4** or **8** with the same alkynes proceed differently since they did not take place at room temperature, but at 90 °C, and resulted in the precipitation of metallic palladium and the formation of the indenones **12a** (R = R′ = Ph; 29%),

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12b (R = R′ = Et; 28%), **12c** (R = Ph, R′ = Me; 26%) or **13a** (R = R′ = Ph; 83%), **13b** (R = R′ = Et; 94%), **13c** (R = Ph, R′ = Me; 62%) (Scheme 2), respectively. The synthesis of the indenone **13a** has been reported by reacting diphenylacetylene with 2-iodobenzonitrile[11] or 2-iodobenzaldehyde or 2-bromobenzaldehyde[1] using a palladium catalyst or diphenylacetylene with benzoyl chloride using $[RhCl(cod)]_2$ as catalyst.[12] The last method has also been used to prepare **13b** and a mixture of both regioisomers of **13c**.[12] Reactions of *o*-diiodobenzene with the same alkynes we used in this work and $[Ni(CO)_4]$ led to the indenones **13**, although **13c** was obtained along with its regioisomer.[5] In our case, the compounds **12c** and **13c** were the only regioisomers formed.

We have also studied the reaction of the neutral 2-acetylphenylpalladium complex **7** with Tl(TfO) or the cationic **9** with MeC≡CPh. The results are similar to those obtained from **2** or **6**, and the corresponding indenols can be isolated [**14a** (R = R′ = Ph; 70%), **14b** (R = R′ = Et; 67%),[17,27] **14c** (R = Ph, R′ = Me; 78%)]. The spectroscopic data of **14a** and **14b** were identical to those previously obtained by reacting $[Mn\{\kappa^2\text{-}C,O\text{-}C_6H_4C(O)Me\text{-}2\}(CO)_4]$ with Me_3NO and the corresponding alkynes.[17] The synthesis of **14a** has also been reported by reacting 2-bromoacetophenone with diphenylacetylene using $Pd(OAc)_2$ as catalyst. When in this reaction PhC≡CMe was used, a mixture of both regioisomers (48:20) was obtained.[20,22] A 1:1 mixture of both regioisomers was also obtained by reacting benzoyl chloride with PhC≡CMe using $[RhCl(cod)]_2$ as catalyst.[12] The mixture was not separated. In our case, the reaction with PhC≡CMe is regioselective, giving the isomer **14c** with the Me substituent at the 3 position (see Scheme 2 and Chart 1).

Characterization of Indenols and Indenones. The IR spectra of the new indenols show one band at 3500−3250 cm^{-1} assignable to the ν(OH), although in **10b** two bands are observed (3284 and 3188 cm^{-1}). This is a solid state effect since in solution only one group of signals appears in its ^1H NMR spectrum. The indenones **12a**, **12b**, and **12c** show bands at 1720−1700 cm^{-1} corresponding to the ν(C═O) mode of the keto group. The absorptions assignable to the $\nu_{assym}(NO_2)$ mode appear at about 1520 cm^{-1} for the indenols and at slightly higher frequencies, 1525−1540 cm^{-1}, for the indenones due to the different electronic effects of OH and NO_2. The $\nu_{sym}(NO_2)$ appears in all cases around 1345 cm^{-1}.

The ^1H NMR spectra of the indenols **10a** and **10b** show two doublets assignable to the methine proton C*H*OH and to the OH. The C*H*OH proton of **10c** appears as a doublet of quadruplets because it is coupled with the OH [^2J(HH) = 8 Hz] and with the Me group ^5J(HH) = 2 Hz.

In the case of **10c**, **11c**, **12c**, and **14c** the relative positions of the Me and the Ph groups have been determined by NOE experiments. The spectroscopic data of **13c** coincide with those previously reported.[5] Irradiation of the OH proton in **10c** exerts a positive NOE over the aryl H7 (weak) (see numbering in Chart 1) and the methine C*H*OH (medium). Irradiation of C*H*OH gives positive NOE at H7 (weak) and some of the Ph protons (weak). Irradiation of the Me substituent causes positive NOE on the aryl H4 (strong) and the Ph protons (weak) (Scheme 2) as the only regioisomer. In the case of **11c**, irradiation of the signal corresponding to the methyl substituent causes medium positive NOE on two different aryl protons, possibly H4 (Chart 1) and the *ortho* protons of the phenyl substituent, which seems to point to the proposed structure. However, irradiation on the OH and C*H*OH did not give conclusive results, and for this reason we decided to confirm the structure by means of a C−H long-range correlation. In the resulting spectrum (Figure 1) it was possible to see intense cross-peaks due to two-bond and three-bond couplings, and in some cases very weak cross-peaks due to four-bond couplings. Between the methyl protons and the CHOH carbon there is just one of these weak peaks, which suggests that they are separated by four bonds. Furthermore, there is another four-bond coupling between the methyl protons and one aryl CH carbon, as well as three strong cross-peaks [^2J(CH) or ^3J(CH)] between the same protons and quaternary aromatic carbons, both results being only compatible with the suggested structure with the Me substituent at the 3 position. The structure of **12c** was also confirmed by NOE experiments. Irradiation of the signal at 2.43 ppm corresponding to the Me group causes positive NOE on the Ph protons (weak) and on H4 (strong). Irradiation at ca. 7.4 ppm (Ph protons) gives positive medium NOE on the Me substituent. Irradiation at 7.99 ppm (H4) gives weak positive NOE on the Me group. In **14c**, there are two ^1H NMR signals corresponding to methyl groups at 2.10 and 1.51 ppm. On irradiation of the former, positive NOE is observed on two different aryl protons (7.55 and 7.26 ppm, medium). Irradiation of the later causes also positive NOE in the aromatics region (7.55 and 7.46 ppm, medium); this is only compatible with the proposed structure, the signals at 2.10 and 1.51 ppm being assigned to Me-3 and Me-1, respectively, and the aromatic signals at 7.26, 7.46, and 7.55 ppm to H4, H7, and the *ortho* protons of the Ph-2 group, respectively. This is confirmed by a C−H long-range correlation experiment (Figure 2) which does not show any cross-coupling between the Me-3 protons and the alcoholic carbon (C1). Moreover, there are three cross-couplings due to two ^3J(CH) and one ^2J(CH) between the protons

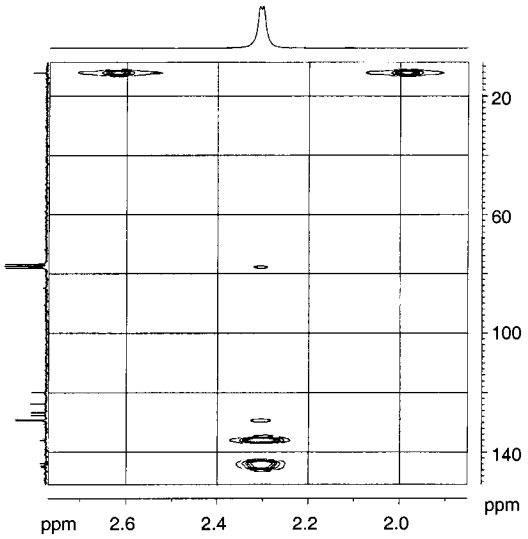


Figure 1. C−H long-range correlation spectrum of **11c**.

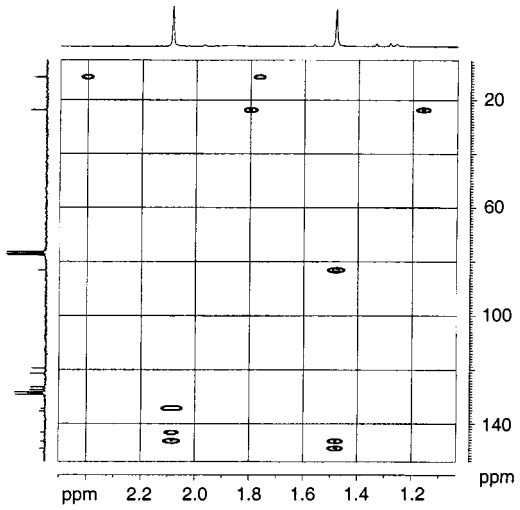


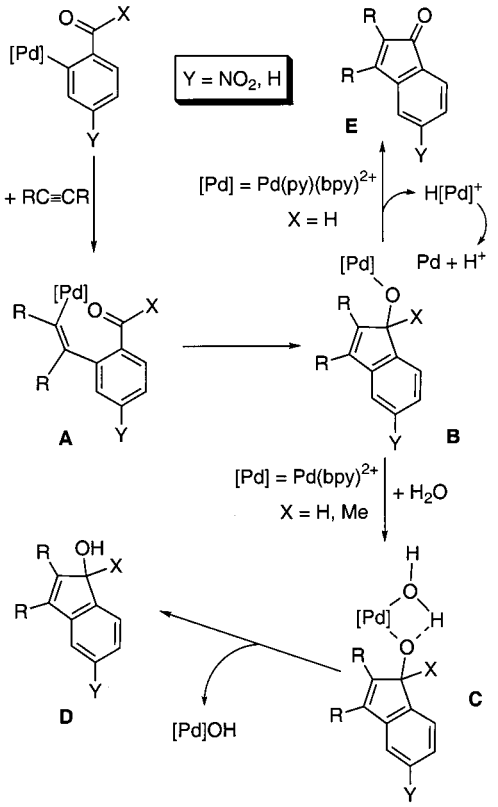
Figure 2. C−H long-range correlation spectrum of **14c**.

of the Me-3 and quaternary aromatic carbons (in the alternative structure there would be only two). It is also possible to see the ^2J(CH) correlation between the protons of the Me-1 and the alcoholic C1, which confirms the assignment of the methyl resonances. The assignment of the methyl signals in the ^{13}C NMR can be made through the ^1J couplings, which are also observable in this experiment, and they are in accordance with the corresponding spectra of **11a**, **14a**,[17] and **14b**.[17]

Discussion

We have previously shown that the trimethoxyarylpalladium(II) complexes [Pd{$C_6H(OMe)_3$-2,3,4-(CHO)-6}(TfO)(bpy)] and [Pd{$C_6H(OMe)_3$-2,3,4-(C[O]Me)-6}-(TfO)(bpy)] react with alkynes to give indenols or indenones depending on the reaction conditions (see Introduction). We proposed plausible reaction pathways to give account of these results.[23] The results we describe here provide more data in order to understand such reactions. Thus, the reactions of the formylaryl complex **2** or **6** with the three tested alkynes in the presence of Tl(TfO) gave indenols **10** or **11** after removing the insoluble mixture containing TlI and [$Pd_2(\mu$-$OH)_2(bpy)_2$](TfO)$_2$ (Scheme 2). We propose that these indenols are formed following the steps depicted in Scheme 3, route **A**−**D**. (i) Insertion of the alkyne into the palladium−carbon bond to give a vinylpalladium intermediate (**A**). The removing of the bromo ligand facilitates the coordination of the alkyne, which is a previous step to the insertion reaction.[36] Monoinserted complexes of this type have been isolated[25,26,37] or postulated as intermediates in metal-mediated organic synthesis.[11,38,39] (ii) Insertion of a Pd−C bond across the carbonyl group leading to a palladium indenolato complex (**B**). Similar species have been isolated by reacting a cyclopalladated phenyl 2-pyridyl ketone complex with alkynes.[40] (iii) Formation of the aquo complex **C** with

Scheme 3. Proposed Reaction Pathway for the Stoichiometric Synthesis of Indenols and Indenones 10−14



adventitious water and hydrolysis to give the indenol (**D**) and [$Pd_2(\mu$-$OH)_2(bpy)_2$](TfO)$_2$. The formation of 1-methylindenols from complex **7** may take place in a similar manner. We have previously shown that under anhydrous conditions similar reactions lead to indenones and palladium metal.[23] A different reaction pathway for the formation of indenones by treating 2-iodo- or 2-bromobenzaldehyde with various alkynes in the presence of [Pd(OAc)$_2$] as catalyst involves an oxidative insertion into the aldehyde C−H bond to form a hydrido palladium(IV) intermediate.[1] However, there does not appear to be any precedent for such an oxidative addition step.

By reacting together [Hg(Ar^1)$_2$] [Ar^1 = $C_6H(OMe)_3$-2,3,4-(CHO)-6], Ph_2C_2, and $CuCl_2$ (as reoxidant) in the presence of [Pd_2Cl_6]$^{2-}$ as catalyst we preliminarily reported in 1992 the catalytic synthesis of the corresponding indenol (62% yield).[28] Later,[23] we reported (i) that the same reaction in freshly distilled Me_2CO, under nitrogen, gave a spiro compound, C_6Ph_6, and Ar^{1}Cl; (ii) that the synthesis of the same indenol can also be made catalytic in copper using oxygen as the reoxidant (52% yield); and (iii) that the reaction of $IC_6H(OMe)_3$-2,3,4-{C(O)Me}-6 with Ph_2C_2 in the presence of a mixture of Pd(OAc)$_2$, PPh_3, and NEt_3 (DMF at 100 °C) gives 22%

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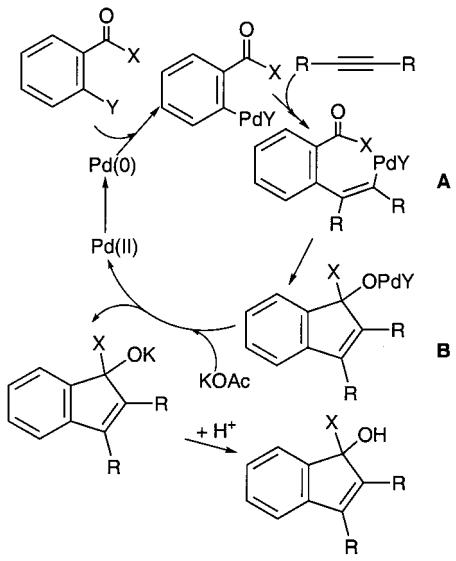
Scheme 4. Mechanism Proposed by Yamamoto et al. for the Catalytic Synthesis of Indenols



of the corresponding indenol.[41] The last reaction conditions follow those of Larock's palladium-catalyzed synthesis of indenones from *o*-halobenzaldehyde and alkynes.[1] Yamamoto et al. have recently proposed a mechanism for the palladium-catalyzed synthesis of indenols (Scheme 4)[20,22] having intermediates **A** and **B** (Scheme 4) in common with what we reported previously for the stoichiometric reaction (Scheme 3).[23,28] However, the next steps in the proposed mechanism are different from those in Scheme 3, probably because the catalytic reactions were carried out under anhydrous conditions, at high temperatures, and in the presence of a base. Nevertheless, there are some unclear steps in this mechanism.[20] First, the Pd(II) complex obtained in the reaction between KOAc and the palladium indenolate evolves to Pd(0) without the concomitant oxidation process any reduction requires. Second, KOAc is used as a base although the proposed catalytic cycle does not seem to demand a base but a potassium salt. And third, the suggested last step leading to the indenol requires one mole of acid per mole of indenol instead of a base.

A different behavior was observed starting from the cationic complexes **4** and **8**. First, there is no reaction with the alkynes at room temperature. Probably, the presence of the pyridine ligand prevents coordination of the alkyne and, therefore, the insertion reaction to give **A**. On heating at 90 °C for a long period of time (19−72 h), such insertion could occur to give the indenolato complex **B**. The presence of the pyridine ligand blocks the coordination position from being occupied by water, preventing the hydrolytic process and formation of the indenol. Decomposition of the indenolato complex through a β-hydrogen elimination seems to occur on heating, giving metallic palladium and the indenones **12** and **13** (**E**, Scheme 3). In the processes of oxidation of alcohols to carbonyl compounds using palladium complexes, it has been proposed the formation of related alkoxo intermediates which evolved through a β-hydrogen elimination to carbonyl compounds and a hydrido-palladium(II) complex which decomposes to Pd(0) and H^+.[42,43] In our case, the decomposition reaction gives pyridine and bipyridine that can remove the H^+ to give the corresponding salts. In addition, it has also been proposed that some alkoxo-palladium complexes decompose through a similar β-elimination process.[44,45] The presence of the pyridine ligand probably prevents the formation of the intermediate **C** from **B**, and this reaction follows a reaction pathway different from that leading to the indenols **10**, **11**, and **14** from the neutral complexes **2**, **6**, and **7**, respectively. In the reactions starting from the 2-formylphenyl complex **6**, the indenols **11** were accompanied by traces of the corresponding indenones **13** (8−15%), while the 2-formyl-5-nitrophenyl complex **2** leads only to the indenols **10**. These facts imply that starting from the neutral complex **6**, the route **A** → **B** → **E** competes, although irrelevantly, with the main pathway **A** → **D**. Because some methoxy-substituted arylpalladium complexes also behave as the 2-formyl-5-nitrophenyl complex **2**,[23] it seems that there is no correlation between the electron-withdrawing effect of the nitro group and its different behavior from that of complex **6.**

The cationic complex **9** behaves differently from **4** and **8**. Thus, it reacts at room temperature (16 h) with PhC≡CMe to give the indenol **14c** and $[Pd_2(\mu\text{-}OH)_2(bpy)_2](TfO)_2$. If our reaction pathway is right, this difference could be due to an easier replacement of pyridine by the alkyne in **9** than in **4** and **8**. The hydrolytic step **B** → **C** would be preferred to the step **B** → **D**, which would require a C−C instead of a C−H bond cleavage. This reaction was also studied in the same conditions as its homologous **4** and **8** (90 °C, 20 h, 51% yield). The indenol **14c** was also obtained, but instead of the byproduct $[Pd_2(\mu\text{-}OH)_2(bpy)_2](TfO)_2$, palladium metal was formed.

An unsymmetrical alkyne, PhC≡CMe, has been tested in the reactions of **2**, **4**, **6**, **7**, **8**, and **9** with alkynes. In all cases only one of the two possible regioisomers is detected and isolated, that with the phenyl substituent at the 2 position (Scheme 2 and Chart 1). Such regioselectivity of alkyne into Pd−C bonds has many precedents,[46] but, as mentioned above, it is not observed in metal-assisted catalytic syntheses of indenols[12,20] or indenones.[1] We have previously discussed the regioselectivity of the insertion of alkynes into Pd−C bonds and have proposed the following empirical scale giving the tendency of a CR group to be bonded to C_{Pd} (the 3 position in our case):[38]

$$CO_2Et \approx CHO \approx C(O)Me \approx SO_2C_6H_4Me\text{-}4 \geq H > Me \approx Et > aryl > Bu^t \approx SiR_3$$

(41) Failing to reference these results, Yamamoto et al. have recently reported a preliminary communication on "the first examples of palladium-catalyzed nucleophilic cyclic vinylpalladation of aryl ketones with alkynes to produce indenols in good to high yields".[20]Although they later wrote a correction giving account of our stoichiometric reactions,[22] they ignored we had also reported some catalytic synthesis of indenols in the same publications we reported the stoichiometric ones.[23,28] The same omissions were found in another preliminary letter reporting new examples of the same catalytic process.[21]

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The results found in the present work are in agreement with this scale.

Conclusions

The method we described for the first time to prepare dipalladated terephthaldehyde complexes (cyclometalation of the corresponding imine followed of a hydrolytic reaction) has now been successfully applied to prepare the first 2-formyl-5-nitrophenyl complexes. The reactions of neutral complexes [Pd{$C_6H_4C(O)X$-2-Y-5}Br(bpy)] (X = H, Y = H, NO_2; X = Me, Y = H) with internal alkynes and Tl(TfO) give indenols, whereas cationic complexes [Pd{C_6H_4CHO-2-Y-5}(py)(bpy)](TfO) (Y = H, NO_2) react with alkynes to give indenones. The results can be explained using a reaction pathway we reported previously for trimethoxyarylpalladium complexes. The electronic properties of the aryl substituents do not significantly change the results. The reactions with MeC≡CPh are regioselective.

Experimental Section

The reactions were carried out without precautions to exclude atmospheric moisture. The IR (solid state, Nujol/polyethylene) and C, H, and N analyses, conductivity measurements in acetone, and melting point determinations were carried out as described elsewhere.[47] Unless otherwise stated, NMR spectra were recorded in $CDCl_3$ in a Varian Unity 300 or a Bruker Unity 200. Chemical shifts were referred to TMS [^{1}H and ^{13}C(^{1}H)] and H_3PO_4 [^{31}P]. The syntheses of **6**, **7**, **14a**, and **14b**[27] were reported previously.

Synthesis of [Pd$_2${κ^2-C,N-C_6H_3(CH=NBu)-2-(NO_2)-5}$_2$-(μ^2-OAc)$_2$] (1). A mixture of 4-nitrobenzaldehyde (1 g, 6.7 mmol) and *n*-butylamine (0.49 g, 6.7 mmol) in MeCN (16 cm^3) was stirred at room temperature for 24 h. The solvent was evaporated in vacuo and the residue extracted with *n*-hexane (20 cm^3). The extract was filtered over anhydrous $MgSO_4$ and the resulting solution evaporated in vacuo to dryness and then heated in vacuo for 8 h at 70 °C. The imine BuN=CHC_6H_4-NO_2-4 is thus obtained as a yellow oil (1.1 g, 81%). BuN=$CHC_6H_4NO_2$-4 (1.1 g, 5.3 mmol) and $Pd(OAc)_2$ (0.89 g, 4 mmol) were mixed in toluene (80 cm^3) and refluxed for 5 h in a Soxhlet system having CaH_2 in the extraction thimble. The solvent was removed in vacuo, and the residue was washed with *n*-hexane (3 × 10 cm^3) and recrystallized from CH_2Cl_2/Et_2O to give red **1**. Yield: 1.2 g, 83%. Mp: 220 °C (dec). Anal. Calcd for $C_{26}H_{32}N_4O_8Pd_2$: C, 42.12; H, 4.35; N, 7.56. Found: C, 42.39; H, 4.29; N, 7.47. IR (cm^{-1}): ν(NO_2), 1518, 1342; ν(C=N) and ν(C=O), 1574−1556 (br). ^{1}H NMR (200 MHz, $CDCl_3$): 7.88−7.83 (m, 2H, CH), 7.37 (s, 1H, CH), 7.15, (d, 1H, ^3J(HH) = 8 Hz, CH), 3.4−3.25 (m, 1H, CH_2), 2.85−2.65 (m, 1H, CH_2), 2.21 (s, 3H, COMe), 1.9−1.4 (m, 2H, CH_2), 1.4−1.05 (m, 2H, CH_2), 0.88 (t, 3H, ^3J(HH) = 7.5 Hz, CH_2*Me*).

Synthesis of [Pd{C_6H_3(CHO)-2-(NO_2)-5}Br(bpy)] (2). To a suspension of **1** (400 mg, 0.54 mmol) in 3:1 Me_2CO/H_2O (28 cm^3) were added NaBr (545 mg, 5.38 mmol), 2,2′-bipyridine (bpy) (168 mg, 1.07 mmol), and acetic acid (ca. 3.5 cm^3), and the resulting mixture was stirred at room temperature for 15 h. The solvents were evaporated in vacuo, leaving a residue, which was extracted with CH_2Cl_2 (20 cm^3). The extract was filtered over Celite, and the components of the orange filtrate were separated using preparative TLC (silica gel). Elution with 3:1 CH_2Cl_2/Me_2CO gave a yellow band, which was collected and extracted with Me_2CO to give a solution, which was evaporated. The residue was redissolved in CH_2Cl_2 (15 cm^3), and anhydrous $MgSO_4$ was added. The resulting suspension was filtered over $MgSO_4$, and the filtrate was evaporated almost to dryness. Addition of Et_2O (10 cm^3) caused the precipitation of a solid. The suspension was filtered and the solid washed with Et_2O and air-dried, giving yellow complex **2**. Yield: 371 mg, 70%. Mp: 190 °C (dec). Anal. Calcd for $C_{17}H_{12}BrN_3O_3Pd$: C, 41.44; H, 2.46; N, 8.53. Found: C, 41.08; H, 2.39; N, 8.27. IR (cm^{-1}): ν(C=O), 1676. ^{1}H NMR (300 MHz, DMSO-d_6): 11.06 (s, 1 H, CHO), 9.18 (dd, 1 H, ^3J(HH) = 4 Hz, ^4J(HH) = 2 Hz, H6 bpy), 8.64 (d, 2 H, ^3J(HH) = 8 Hz, H3 and H3′ bpy), 8.45 (d, 1 H, ^3J(HH) = 2 Hz, H6 aryl), 8.5−8.2 (several m, 2 H, H4 and H4′ bpy), 7.93 (dd, 1 H, ^3J(HH) = 8 Hz, ^4J(HH) = 2 Hz, H4 aryl), 7.9−7.8 (several m, 2 H, H5 bpy and H3 aryl), 7.6−7.5 (m, 2 H, H6′ and H5′ bpy). ^{13}C NMR (50 MHz, DMSO-d_6): 195.26 (CHO), 160.98 (C−Pd), 156.08 (C2 or C2′ bpy), 153.98 (C2′ or C2 bpy), 150.26 (C6 or C6′ bpy), 149.41 (C6′ or C6 bpy), 147.70 (C5 or C2 aryl), 145.35 (C2 or C5 aryl), 140.45 (C4 or C4′ bpy), 140.35 (C4′ or C4 bpy), 130.50 (C6 aryl), 127.74 (CH aryl or C5 or C5′ bpy), 127.44 (CH aryl or C5 or C5′ bpy), 127.32 (CH aryl or C5′ or C5 bpy), 123.85 (C3 and C3′ bpy), 118.76 (C4 aryl).

Synthesis of *trans*-[Pd{C_6H_3(CHO)-2-(NO_2)-5}Br(PPh_3)$_2$] (3). Complex **3** was similarly prepared and purified as **2** by reacting **1** (100 mg, 0.13 mmol), NaBr (138 mg, 1.34 mmol), PPh_3 (141 mg, 0.54 mmol), and acetic acid (ca. 1.5 cm^3) in Me_2CO/H_2O (5:2, 14 cm^3). Yield: 139 mg, 60%. Mp: 186 °C (dec). Anal. Calcd for $C_{43}H_{34}BrNO_3P_2Pd$: C, 59.89; H, 3.98; N, 1.62. Found: C, 59.69; H, 3.88; N, 1.62. IR (cm^{-1}): ν(C=O), 1686. ^{1}H NMR (300 MHz, $CDCl_3$): 10.19 (s, 1 H, CHO), 8.0−7.0 (several m, 32 H), 6.86 (d, 1 H, ^3J(HH) = 8 Hz, aryl). ^{13}C NMR (50 MHz, $CDCl_3$): 193.55 (CHO), 173.71 (t, ^2J(PC) = 5 Hz, C-Pd), 147.65 (C5 aryl), 143.88 (t, ^3J(PC) = 2 Hz, C2 aryl), 134.48 (apparent t, $|^2J(PC) + {}^4J(PC)|$ = 12 Hz, *ortho* C's PPh_3), 130.63 (t, ^3J(PC) = 4 Hz, C6 aryl), 130.53 (CH aryl), 130.36 (*para* C's PPh_3), 130.16 (apparent obscured t, *ipso* C's PPh_3), 128.23 (apparent t, $|^3J(PC) + {}^5J(PC)|$ = 10 Hz, *meta* C's PPh_3), 117,26 (CH aryl). ^{31}P NMR (121 MHz, $CDCl_3$): 24.04.

Synthesis of [Pd{C_6H_3(CHO)-2-(NO_2)-5}(py)(bpy)](TfO) (4). Pyridine (9 mg, 0.12 mmol) and Tl(TfO) (TfO = CF_3SO_3) (43 mg, 0.12 mmol) were added to a solution of **2** (60 mg, 0.12 mmol) in CH_2Cl_2 (15 cm^3), and the resulting mixture was stirred for 1 h at room temperature. The suspension was filtered over Celite, the filtrate was evaporated to dryness, and Et_2O (8 cm^3) was added. The suspension was filtered, and the solid was washed with Et_2O (3 × 4 cm^3) and air-dried to give **4** as a white solid. Yield: 68 mg, 87%. Mp: 137 °C. Anal. Calcd for $C_{23}H_{17}F_3N_4O_6PdS$: C, 41.70; H, 2.68; N, 8.74; S, 5.00. Found: C, 42.47; H, 2.28; N, 8.72; S, 4.95. IR (cm^{-1}): ν(C=O), 1688. Λ_M (Ω^{-1} cm^2 mol^{-1}): 122. ^{1}H NMR (200 MHz, DMSO-d_6): 10.99 (s, 1 H, CHO), 9.06 (d, 2 H, J(HH) = 5 Hz), 8.85 (d, 1 H, J(HH) = 2 Hz), 8.8−8.7 (m, 2 H), 8.5−8.2 (m, 2 H), 8.15−7.85 (several m, 3 H), 7.8−7.65 (m, 3 H), 7.6−7.5 (m, 3 H). ^{13}C NMR (50 MHz, DMSO-d_6): 195.18 (CHO), 162.33 (C-Pd), 156.42, 153.84 (C2′ and C2 bpy), 152.33 (*ortho* CH's py), 151.87 (C6 or C6′ bpy), 148.43 (C2 or C5 aryl), 148.10 (C6′ or C6 bpy), 145.31 (C5 or C2 aryl), 141.47, 140.35 (C4, C4′ bpy and *para* CH py), 131.22 (C4 aryl), 129.57, 128.33, 128.27 (C5, C5′ bpy and C3 aryl), 127.51 (*meta* CH's py), 124.45, 123.86 (C3 and C3′ bpy), 120.22 (C6 aryl).

Synthesis of [Pd{C_6H_3(CHO)-2-(NO_2)-5}(bpy)(PPh_3)](TfO) (5). The yellow complex **5** was similarly prepared from **2** (100 mg, 0.20 mmol), PPh_3 (53 mg, 0.20 mmol), and Tl(TfO) (72 mg, 0.20 mmol). Yield: 136 mg, 81%. Mp: 208 °C. Anal. Calcd for $C_{36}H_{27}F_3N_3O_6PPdS$: C, 52.46; H, 3.30; N, 5.10; S,

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3.89. Found: C, 52.08; H, 3.34; N, 5.16; S, 3.79. IR (cm^{-1}): ν(C═O), 1686. Λ_M (Ω^{-1} cm^2 mol^{-1}): 125. ^{1}H NMR (200 MHz, $CDCl_3$): 9.97 (s, 1 H, CHO), 8.74 (d, 2 H, ^3J(HH) = 8 Hz), 8.34 (t, 1 H, ^4J(HH) = 2 Hz), 8.25 (m, 2 H), 7.89 (dd, 1 H, ^3J(HH) = 8 Hz, ^4J(HH) = 2 Hz), 7.65−7.28 (m, 20 H). ^{13}C NMR (75 MHz, $CDCl_3$): 193.10 (CHO), 163.23 (d, ^2J(PC) = 12 Hz, C-Pd), 155.79, 150.62, 149.01, 148.68, 144.05, 141.74, 135.59, 134.31 (d, ^3J(PC) = 12 Hz, *ortho* C's PPh_3), 132.27 (s, *para* C's PPh_3), 129.63 (d, J(PC) = 5 Hz), 129.34 (d, ^4J(PC) = 11 Hz *meta* C's PPh_3), 127.37 (d, ^1J(PC) = 53 Hz, *ipso* C's PPh_3), 127.05 (d, J(PC) = 51 Hz), 124.94, 119.78. ^{31}P NMR (121 MHz, $CDCl_3$): 31.77.

Synthesis of [Pd{C_6H_4(CHO-2}(py)(bpy)](TfO) (8). Pyridine (0.2 cm^3, 2.5 mmol) and Tl(TfO) (789 mg, 2.23 mmol) were added to a solution of **6** (1000 mg, 2.23 mmol) in CH_2Cl_2 (30 cm^3), and the mixture was stirred at room temperature for 16 h. The resulting suspension was filtered over Celite, the filtrate was evaporated to dryness, and the residue was triturated with Et_2O. The suspension was filtered and the solid washed with Et_2O to give yellow **8**. Yield: 1.26 g, 95%. Mp: 96−98 °C. Anal. Calcd for $C_{23}H_{18}F_3N_3O_4PdS$: C, 46.36; H, 3.04; N, 7.05; S, 5.38. Found: C, 46.62; H, 3.47; N, 6.72; S, 5.18. IR (cm^{-1}): ν(C═O), 1692. Λ_M (Ω^{-1} cm^2 mol^{-1}): 142. ^{1}H NMR (300 MHz, $CDCl_3$): 10.36 (s, 1 H, CHO), 8.85 (d, 2 H, ^3J(HH) = 5 Hz), 8.52 (t, 2 H, ^3J(HH) = 8 Hz), 8.18−8.15 (m, 2 H), 7.94−7.90 (m, 2 H), 7.70−7.22 (m, 9 H). ^{13}C NMR (50 MHz, $CDCl_3$): 194.82 (CHO), 159.10 (C), 156.50 (C), 153.70 (C), 152.00 (CH), 151.08 (CH), 147.63 (CH), 141.00 (C), 140.92 (CH), 140.82 (CH), 139.64 (CH), 134.98 (CH), 134.76 (CH), 133.39 (CH), 127.72 (CH), 127.06 (CH), 126.95 (CH), 125.33 (CH), 124.15 (CH), 123.75 (CH).

Synthesis of [Pd{C_6H_4(C[O]Me)-2}(py)(bpy)](TfO) (9). Complex **7** (150 mg, 0.32 mmol) was reacted with pyridine (0.026 cm^3, 0.32 mmol) and Tl(TfO) (113 mg, 0.32 mmol) in CH_2Cl_2 (15 cm^3) during 16 h at room temperature. The suspension was filtered over Celite, and the filtrate was evaporated to dryness. The residue was triturated with Et_2O (12 cm^3), the resulting suspension was filtered, and the solid was washed with Et_2O and air-dried, giving yellow **7**. Yield: 179 mg, 92%. Mp: 158 °C (desc). Anal. Calcd for $C_{24}H_{20}F_3N_3O_4$-PdS: C, 47.26; H, 3.31; N, 6.89; S, 5.26. Found: C, 46.79; H, 3.18; N, 6.89; S, 5.07. IR (cm^{-1}): ν(C═O), 1658. Λ_M (Ω^{-1} cm^2 mol^{-1}): 150. ^{1}H NMR (300 MHz, $CDCl_3$): 8.81−8.79 (m, 2 H, *ortho*-H py), 8.29 (bd, 2 H, ^3J(HH) = 8 Hz, H3 and H3′ bpy), 8.08 (bt, 2 H, ^3J(HH) = 8 Hz, H4 and H4′ bpy), 7.86 (tt, 1 H, ^3J(HH) = 8 Hz, ^4J(HH) = 2 Hz, *para*-H py), 7.69 (bd, 2 H, ^3J(HH) = 7 Hz, H3 and H6 aryl), 7.46−7.41 (m, 2 H, *meta*-H py), 7.23 (bt, 1H, aryl), 7.10 (td, 1 H, ^3J(HH) = 8 Hz, ^4J(HH) = 1 Hz, aryl), 2.54 (s, 3 H, Me). ^{1}H NMR (300 MHz, $CDCl_3$, TMS, −60 °C): 8.97−8.91 (m, 2 H), 8.61 (t, 2H, ^3J(HH) = 8 Hz), 8.29−8.18 (m, 2 H), 8.02 (t, 1 H, ^3J(HH) = 8 Hz), 7.92 (t, 2H, ^3J(HH) = 7 Hz), 7.65 (1H, bt, ^3J(HH) = 7 Hz), 7.60−7.55 (m, 2H), 7.45 (d, 1 H, J(HH) = 4), 7.4−7.3 (m, 3H), 7.23 (t, 1H), 2.73 (s,3 H, Me).

Synthesis of 5-Nitro-2,3-diphenyl-1*H*-inden-1-ol (10a). Complex **2** (400 mg, 0.81 mmol), Tl(TfO) (287 mg, 0.81 mmol), and diphenylacetylene (431 mg, 2.44 mmol) were reacted in CH_2Cl_2 (20 cm^3) for 15 h. The suspension was filtered over Celite, and the filtrate was concentrated to dryness. The residue was extracted with Et_2O (30 cm^3) and filtered. Preparative TLC (silica gel) was used to separate the mixture. The yellow band was collected, the product extracted with Me_2-CO, and the corresponding solution evaporated to dryness. The residue was dissolved in CH_2Cl_2 (15 cm^3) and treated with anhydrous $MgSO_4$ for 1 h. The suspension was filtered, the filtrate was evaporated almost to dryness, and *n*-hexane was added. The resulting suspension was filtered, and the precipitate was washed with *n*-hexane (3 × 4 cm^3) and air-dried to give **10a** as a yellow solid. Yield: 179 mg, 67%. Mp: 140 °C. Anal. Calcd for $C_{21}H_{15}O_3N$: C, 76.58; H, 4.60; N, 4.25. Found: C, 76.34; H, 4.63; N, 4.25. IR (cm^{-1}): ν(OH), 3484, ν(NO_2), 1522, 1342. ^{1}H NMR (300 MHz, $CDCl_3$): 8.18 (dd, 1 H, ^3J(HH) = 8 Hz, ^4J(HH) = 2 Hz, H6), 7.96 (d, 1 H, ^4J(HH) = 2 Hz, H4), 7.77 (d, 1 H, ^3J(HH) = 8 Hz, H7), 7.5−7.2 (m, 10 H), 5.76 (d, 1 H, ^3J(HH) = 8 Hz, C*H*OH), 2.01 (d, 1 H, ^3J(HH) = 8 Hz, CHO*H*). ^{13}C NMR (75 MHz, $CDCl_3$): 150.61 (C), 149.09 (C), 146.39 (C), 145.48 (C), 138.14 (C), 132.96 (C), 129.92 (C), 129.25 (CH, Ph), 128.82 (CH, Ph), 128.53 (CH, Ph), 128.50 (CH, Ph), 128.28 (CH, Ph), 128.15 (CH, Ph), 124.11 (CH, C6), 121.88 (CH, C7), 115.36 (CH, C4), 76.74 (CH, CHOH). MS: *m*/*z*, 329 (M^+, 100%), 283 ($M^+ - NO_2$ 17%), 252 (M^+ − Ph, 64%), 77 (Ph, 23%).

Synthesis of 2,3-Diethyl-5-nitro-1*H*-inden-1-ol (10b). Complex **2** (200 mg, 0.41 mmol), Tl(TfO) (143 mg, 0.41 mmol), and 3-hexyne (100 mg, 1.21 mmol) were mixed in CH_2Cl_2 (20 cm^3) and stirred for 1 h. The suspension was filtered over Celite, and the filtrate was evaporated to dryness. The residue was extracted with Et_2O (15 cm^3) and the extract filtered over Celite. The filtrate was concentrated to ca. 2 cm^3 and cold *n*-hexane (−10 °C, 4 cm^3) added, causing the precipitation of a yellow solid, which was filtered, washed with cold *n*-hexane (−10 °C, 1 cm^3), and air-dried, giving yellow **10b**. A further amount of **10b** can be obtained by evaporation of the mother liquors and precipitation with cold *n*-hexane (−10 °C). Total yield: 61 mg, 64%. Mp: 95 °C. Anal. Calcd for $C_{13}H_{15}O_3N$: C, 66.93; H, 6.49; N, 6.00. Found: C, 66.19; H, 6.35; N, 5.79. IR (cm^{-1}): ν(OH), 3284, 3188; ν(NO_2), 1522, 1342. ^{1}H NMR (300 MHz, $CDCl_3$): 8.05 (dd, 1 H, ^3J(HH) = 8 Hz, ^4J(HH) = 2 Hz, H6), 7.94 (d, 1 H, ^4J(HH) = 2 Hz, H4), 7.58 (d, 1 H, ^3J(HH) = 8 Hz, H7), 5.07 (d, 1 H, ^3J(HH) = 10 Hz, C*H*OH), 2.6−2.4 (m, 4 H, 2×*ABX*$_3$, 2×CH_2), 1.66 (d, 1 H, ^3J(HH) = 10 Hz, CHO*H*), 1.19 (t, 3 H, ^3J(HH) = 7 Hz, Me), 1.17 (t, 3 H, ^3J(HH) = 7 Hz, Me). ^{13}C NMR (75 MHz, $CDCl_3$): 151.68 (C), 148.98 (C), 148.85 (C), 145.53 (C), 137.94 (C), 123.27 (CH, C6), 120.84 (CH, C7), 113.23 (CH, C4), 76.28 (CH, CHOH), 18.82 (CH_2), 18.17 (CH_2), 14.16 (Me), 13.13 (Me). MS: *m*/*z*, 233 (M^+, 36%), 204 (M^+ − Et, 100%).

Synthesis of 3-Methyl-5-nitro-2-phenyl-1*H*-inden-1-ol (10c). Complex **2** (100 mg, 0.20 mmol), Tl(TfO) (71 mg, 0.20 mmol), and phenylmethylacetylene (70 mg, 0.60 mmol) were mixed in CH_2Cl_2 (15 cm^3) and stirred for 2 h. The suspension was filtered over Celite and the filtrate evaporated to dryness. The residue was redissolved in Et_2O (6 cm^3) and the extract filtered over Celite. The filtrate was concentrated to ca. 2 cm^3 and cold *n*-hexane (−10 °C, 4 cm^3) added, causing the precipitation of a solid, which was filtered, washed with cold *n*-hexane (−10 °C, 3 × 4 cm^3), and air-dried, giving yellow **10c**. Yield: 50 mg, 61%. Mp: 129 °C. Anal. Calcd for $C_{16}H_{13}NO_3$: C, 71.89; H, 4.91; N, 5.24. Found: C, 71.53; H, 4.86; N, 5.19. IR (cm^{-1}): ν(OH), 3528; ν(NO_2), 1518, 1350. ^{1}H NMR (300 MHz, $CDCl_3$): 8.16 (dd, 1 H, ^3J(HH) = 8 Hz, ^4J(HH) = 2 Hz, H6), 8.07 (d, 1 H, ^4J(HH) = 2 Hz, H4), 7.69 (d, 1 H, ^3J(HH) = 8 Hz, H7), 7.55−7.3 (m, 5 H, Ph), 5.60 (dq, 1 H, ^3J(HH) = 8 Hz, ^5J(HH) = 2 Hz, C*H*OH), 2.30 (d, 3 H, ^5J(HH) = 2 Hz, Me), 1.84 (d, 1 H, ^3J(HH) = 8 Hz, CHO*H*). ^{13}C NMR (75 MHz, $CDCl_3$): 150.74 (C), 149.24 (C), 146.32 (C), 146.20 (C), 134.24 (C), 133.89 (C), 129.05 (CH, Ph), 128.88 (CH, Ph), 128.08 (CH, *para* C, Ph), 123.71 (CH, C6), 121.88 (CH, C7), 114.24 (CH, C4), 76.91 (CH, CHOH), 11.80(Me). MS: *m*/*z*, 267 (M^+, 100%), 221 ($M^+ - NO_2$, 28%), 252 (M^+ − Me, 37%), 206 ($M^+ - NO_2$ − Me, 20%), 77 (Ph, 23%).

Synthesis of 2,3-Diphenyl-1*H*-inden-1-ol (11a). Complex **6** (889 mg, 1.99 mmol), diphenylacetylene (709 mg, 3.97 mmol), and Tl(TfO) (702 mg, 1.99 mmol) were mixed in CH_2Cl_2 (15 cm^3) and stirred for 16 h at room temperature. The suspension was filtered over Celite, giving a red solution, which was concentrated and applied to silica gel containing ca. 5% fluorescent silica gel. A 1:2 Et_2O/*n*-hexane mixture was used as eluant. Two bands (R_f 0.46 colorless, and R_f 0.71 orange) were collected separately. The corresponding products were extracted with Me_2CO, and the corresponding solutions were dried with $MgSO_4$ for 4 h and, then, filtered. Evaporation to

dryness of these solutions rendered the white indenol **11a** (Rf 0.46) and the red indenone **13a** (R_f 0.71). Yield: **11a**, 293 mg, 52%; **13a**, 46 mg, 8%. The following data are relative to the indenol **11a**. Mp: 124 °C (desc). Anal. Calcd for $C_{21}H_{16}O$: C, 88.40; H, 5.53. Found: C, 88.70; H, 5.67. IR (cm^{-1}): ν(OH), 3456. ^{1}H NMR (300 MHz, $CDCl_3$): 7.61 (1 H, d, ^3J(HH) = 6 Hz), 7.5−7.2 (13 H, m), 5.64 (1 H, d, ^3J(HH) = 8 Hz, C*H*OH), 1.90 (1 H, d, ^3J(HH) = 8 Hz, CHO*H*). ^{13}C NMR (75 MHz, $CDCl_3$): 144.28 (C), 143.86 (C), 143.77 (C), 139.67 (C), 134.74 (C), 134.03 (C), 129.21 (CH), 129.06 (CH), 128.79 (CH), 128.66 (CH), 128.27 (CH), 127.78 (CH), 127.29 (CH), 126.33 (CH), 123.68 (CH), 120.64 (CH), 77.32 (CH, CHOH). MS: *m*/*z*, 284 (M^+, 100%), 207 (M^+ − Ph, 24%).

Synthesis of 2,3-diethyl-1*H*-inden-1-ol (11b). White **11b** was similarly prepared from **6** (800 mg, 1.78 mmol), 3-hexyne (404 μL, 292 mg, 3.56 mmol), and Tl(TfO) (632 mg, 1.78 mmol). A small amount of the indenone **13b** was also isolated. Yield: **11b**, 190 mg, 57% (R_f 0.61); **13b**, 21 mg, 6% (R_f 0.86). The following data are relative to the indenol **11b**. Mp: 66 °C. Anal. Calcd for $C_{13}H_{16}O$: C, 82.90; H, 8.75. Found: C, 82.94; H, 8.57. IR (cm^{-1}): ν(OH), 3204. ^{1}H NMR (300 MHz, $CDCl_3$): 7.43 (d, 1 H, ^3J(HH) =7 Hz), 7.24 (t, 1 H, ^3J(HH) = 7 Hz), 7.15−7.05 (m, 2 H), 4.94 (d, 1 H, ^3J(HH) = 8 Hz, C*H*OH), 2.55−2.3 (m, 4 H, 2×CH_2), 1.68 (d, 1 H, ^3J(HH) = 8 Hz, CHO*H*), 1.14 (t, 6 H, ^3J(HH) = 8 Hz, 2×Me). ^{13}C NMR (75 MHz, $CDCl_3$): 145.83 (C), 145.02 (C), 143.86 (C), 138.74 (C), 128.22 (CH), 124.90 (CH), 123.07 (CH), 118.47 (CH), 76.77 (CHOH), 18.61 (CH_2), 18.22 (CH_2), 14.33 (Me), 13.32 (Me). MS: *m*/*z*, 188 (M^+, 49%), 159 (M^+ − Et, 100%).

Synthesis of 3-Methyl-2-phenyl-1*H*-inden-1-ol (11c). White **11c** was similarly prepared from **6** (500 mg, 1.12 mmol), 1-phenyl-1-propyne (276 μL, 256 mg, 2.24 mmol), and Tl(TfO) (396 mg, 1.12 mmol). A small amount of the indenone **13c** was also isolated. Yield: **11c**, 132 mg, 53% (R_f 0.37); **13c**, 37 mg, 15% (R_f 0.61). The following data are relative to the indenol **11c**. Mp: 90 °C. Anal. Calcd for $C_{16}H_{14}O$: C, 86.40; H, 6.30. Found: C, 86.75; H, 6.61. IR (cm^{-1}): ν(OH), 3242. ^{1}H NMR (300 MHz, $CDCl_3$): 7,6−7.2 (several m, 9 H), 5.55 (bd, 1 H, ^3J(HH) = 9 Hz, C*H*OH), 2.25 (d, 3 H, ^5J(HH) = 2 Hz, Me), 1.64 (d, 1 H, ^3J(HH) = 9 Hz, CHO*H*). ^{13}C NMR (50 MHz, $CDCl_3$): 144.56 (C), 144.23 (C), 143.27 (C), 135.50 (C), 134.94 (C), 128.95 (CH), 128.65 (CH), 128.54 (CH), 127.12 (CH), 126.15 (CH), 123.22 (CH), 119.26 (CH), 77.32 (CH, CHOH), 11.72 (Me). MS: *m*/*z*, 222 (M^+, 98%), 207 (M^+ − Me, 96%).

Synthesis of 5-Nitro-2,3-diphenylinden-1-one (12a). Complex **4** (150 mg, 0.23 mmol) and diphenylacetylene (125 mg, 0.23 mmol) were mixed in 1,2-dichloroethane (20 cm^3) and heated at 80 °C in a closed tube for 72 h. The formation of metallic palladium is observed during the reaction. The final mixture was filtered over Celite. The resultant solution was evaporated to dryness and the residue extracted in Et_2O (15 cm^3), the extract being filtered over Celite. The orange solution was evaporated to almost dryness and cold *n*-hexane (−10 °C) added, causing the precipitation of a solid, which was filtered, washed with cold *n*-hexane (−10 °C, 3 × 4 cm^3), and air-dried, giving orange **12a**. Yield: 29 mg, 29%. Mp: 164 °C. Anal. Calcd for $C_{21}H_{13}NO_3$: C, 77.05; H, 4.01; N, 4.28. Found: C, 76.88; H, 4.01; N, 4.01. IR (cm^{-1}): ν(C═O), 1716; $\nu(NO_2)$, 1538, 1346. ^{1}H NMR (300 MHz, $CDCl_3$): 8.23 (dd, 1 H, ^3J(HH) = 8 Hz, ^4J(HH) = 2 Hz, H6), 7.96 (1 H, d, ^4J(HH) = 2 Hz, H4), 7.73 (d, 1 H, ^3J(HH) = 8 Hz, H7), 7.5−7.25 (10 H, m, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): 194.28 (C═O), 154.23 (C), 151.57 (C), 146.98 (C), 135.25 (C), 134.50 (C), 131.59 (C), 129.78 (C), 130.23 (CH, Ph), 130.04 (CH, Ph), 129.36 (CH, Ph), 128.61 (CH, Ph), 128.41 (2xCH, Ph), 125.30 (CH, C6), 123.15 (CH, C7), 115.83 (CH, C4). MS: *m*/*z*, 327 (M^+, 100%), 252 (M^+ − Ph, 58%), 280 (M^+ − NO_2, 35%).

Synthesis of 2,3-Diethyl-5-nitroinden-1-one (12b). Yellow **12b** was similarly prepared from **4** (150 mg, 0.23 mmol) and 3-hexyne (57 mg, 0.70 mmol) at 90 °C for 72 h. Yield: 15 mg, 28%. Mp: 98 °C. Anal. Calcd for $C_{13}H_{13}O_3N$: C, 67.52; H, 5.67; N, 6.06. Found: C, 67.63; H, 5.68; N, 6.06. IR (cm^{-1}): ν(C═O), 1716; $\nu(NO_2)$, 1530, 1348. ^{1}H NMR (300 MHz, $CDCl_3$): 8.10 (dd, 1 H, ^3J(HH) = 8 Hz, ^4J(HH) = 2 Hz, H6), 7.83 (d, 1 H, ^4J(HH) = 2 Hz, H4), 7.50 (d, 1 H, ^3J(HH) = 8 Hz, H7), 2.63 (q, 2 H, ^3J(HH) = 7.5 Hz, CH_2), 2.33 (q, 2 H, ^3J(HH) = 7.5 Hz, CH_2), 1.26 (t, 3 H, ^3J(HH) = 7.5 Hz, Me), 1.09 (t, 3 H, ^3J(HH) = 7.5 Hz, Me). ^{13}C NMR (75 MHz, $CDCl_3$): 195.72 (C═O), 157.85 (C), 151.48 (C), 146.94 (C), 138.29 (C), 135.64 (C), 124.44 (CH, C6), 121.70 (CH, C7), 113.46 (CH, C4), 19.36 (CH_2), 16.21 (CH_2), 13.74 (Me), 12.18 (Me). MS: *m*/*z*, 231 (M^+, 36%), 202 (M^+ − Et, 100%).

Synthesis of 2-Phenyl-3-methyl-5-nitroinden-1-one (12c). Complex **4** (284 mg, 0.23 mmol) and 1-phenyl-1-propyne (154 mg, 1.32 mmol) were mixed in 1,2-dichloroethane (20 cm^3) and heated at 90 °C in a Carius tube for 24 h. Metallic palladium precipitated during the reaction. The final mixture was filtered over Celite, the filtrate evaporated to dryness, the residue extracted with Et_2O (15 cm^3), and the extract filtered over Celite. The filtrate was concentrated to ca. 5 cm^3. Preparative TLC (silica gel) was used to separate the mixture using 1:1 CH_2Cl_2/*n*-hexane as eluant. The deep yellow band was extracted with Me_2CO, the resulting mixture filtered, and the filtrate evaporated to dryness. The residue was dissolved in CH_2Cl_2 (15 cm^3), treated with solid anhydrous $MgSO_4$ for 1 h, and then filtered. The solution was evaporated to dryness and the residue triturated with cold *n*-hexane (−10 °C, 4 cm^3). The solid was filtered and washed with cold *n*-hexane (−10 °C, 2 × 4 cm^3), yielding orange **12c**. Yield: 31 mg, 26%. Mp: 157 °C. Anal. Calcd for $C_{16}H_{11}NO_3$: C, 72.44; H, 4.18; N, 5.28. Found: C, 72.07; H, 4.18; N, 4.95. IR (cm^{-1}): ν(C═O), 1708; $\nu(NO_2)$, 1528, 1348. ^{1}H NMR (200 MHz, $CDCl_3$): 8.22 (dd, 1 H, ^3J(HH) = 8 Hz, ^4J(HH) = 2 Hz, H6), 7.99 (d, 1 H, ^4J(HH) = 2 Hz, H4), 7.64 (d, 1 H, ^3J(HH) = 8 Hz, H7), 7.55−7.3 (m, 5 H, Ph), 2.43 (s, 3 H, Me). ^{13}C NMR (75 MHz, $CDCl_3$): 194.64 (CHO), 154.25 (C), 152.47 (C), 148.18 (C), 136.44 (C), 135.48 (C), 130.74 (C), 130.20 (CH, Ph), 129.19 (2×CH, Ph), 125.91 (CH, C6), 122.96 (CH, C7), 114.87 (CH, C4), 13.51 (Me). MS: *m*/*z*, 265 (M^+, 100%), 219 (M^+ − NO_2, 23%), 250 (M^+ − Me, 4%), 77 (Ph, 19%).

Synthesis of 2,3-Diphenylinden-1-one (13a). Complex **8** (150 mg, 0.24 mmol) was reacted with diphenylacetylene (134 mg, 0.75 mmol) in 1,2-dichloroethane (10 cm^3) in a closed tube at 90 °C for 20 h. Deposition of metallic palladium was observed during the reaction. The final brown reaction mixture was filtered over Celite, the dark red filtrate was conveniently concentrated, and its components were separated using preparative TLC (silica gel with 5% fluorescent silicagel). A 1:2 Et_2O/*n*-hexane mixture was used as eluant. The orange band (R_f = 0.73) was collected and extracted with Me_2CO. This extract was treated with anhydrous $MgSO_4$ for 1 h. The suspension was filtered and the solution evaporated in vacuo, yielding red **13a**. Yield: 56 mg, 83%. No indenol **11a** was observed. The spectroscopic data (^{1}H and ^{13}C NMR spectra) and melting poing (151−153 °C) coincide with those reported.[48]

Synthesis of 2,3-Diethylinden-1-one (13b). It was similarly prepared [from **8** (150 mg, 0.24 mmol) and 3-hexyne (85 μL, 61 mg, 0.75 mmol)] and purified (yellow band, R_f = 0.86). The indenol **11b** was not detected. Yield: 42 mg, 94%. The spectroscopic data coincide with those previously reported.[5]

Synthesis of 3-Methyl-2-phenylinden-1-one (13c). It was similarly prepared [from **8** (150 mg, 0.24 mmol) and 1-phenyl-1-propyne (93 μL, 0.75 mmol)] and purified (yellow band, eluant 1:1 Et_2O/*n*-hexane, R_f = 0.64). It was isolated as a yellow oil. Yield: 33 mg, 62%. A small amount of indenol **11c** could also be separated (R_f = 0.35; yield: 3 mg, 6%). The spectroscopic data of **13c** coincide with those previously reported.[5]

Synthesis of 1,3-Dimethyl-2-phenyl-1*H*-inden-1-ol (14c). It was prepared as **11c** from **7** (200 mg, 0.44 mmol), 1-phenyl-

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1-propyne (163 μL, 151 mg, 0.88 mmol), and Tl(TfO) (156 mg, 0.44 mmol). The indenol **14c** ($R_f = 0.32$) was isolated as a white solid. Yield: 81 mg, 78%. Mp: 115 °C. Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.82. Found: C, 86.01; H, 6.92; IR (cm^{-1}): ν(OH), 3352. ^{1}H NMR (300 MHz, $CDCl_3$): 7.6−7.2 (several m, 9 H), 2.10 (s, 3 H, Me-3), 1.81 (s, 1 H, OH), 1.51 (s, 3 H, Me-1). ^{13}C NMR (75 MHz, $CDCl_3$): 149.18 (C), 146.47 (C), 143.29 (C), 135.23 (C), 134.29 (C), 129.09 (CH), 128.51(CH), 128.18 (CH), 127.29 (CH), 126.38 (CH), 121.32 (CH), 119.35 (CH), 83.09 (COH), 23.66 (Me-1), 11.48 (Me-3). MS: *m*/*z*, 236 (M^+, 90%), 221 ($M^+ - Me$, 100%), 219 ($M^+ - OH$, 16%).

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