Intramolecular Carbo- and Heterocyclization Induced by Systematic Demetalation of (η^3-Butadienyl)palladium Complexes

Michel Pfeffer* and Jean-Pascal Sutter

Laboratoire de Synthèses Métallo-induites (URA 416 du CNRS), Université Louis Pasteur, 4, rue Blaise Pascal, F-67070 Strasbourg Cédex, France

André DeCian and Jean Fischer

Laboratoire de Cristallochimie et Chimie Structurale (URA 424 du CNRS), Université Louis Pasteur, 4, rue Blaise Pascal, F-67070 Strasbourg Cédex, France

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The treatment of organopalladium complexes containing a polysubstituted butadienyl group η^3-bound to Pd, [N⌒C—C(R^1)=C(R^2)—C(R^3)=C(R^4)—PdCl], with PPh_3 in methanol, led to palladium-free compounds in several instances. These depalladation reactions afforded selectively carbo- and heterocyclic products whose nature was only dependent upon the substituents of the butadienyl fragment.

The formation of carbon–carbon bonds within the coordination sphere of a transition metal is a very appealing aspect of organometallic chemistry since it may provide new pathways for organic synthesis, even though in many instances these reactions are stoichiometric. However, this useful behavior is frequently hampered by the high stability of the organometallic intermediates. To obviate this problem, it would be very interesting to develop demetalation processes that could occur under mild conditions and which would enable the selective synthesis of metal-free organic products. We, and others, have described on many occasions how several carbon–carbon bonds can be formed via stepwise insertion of one to three alkynes into the Pd–C bond of various cyclopalladated starting compounds.[1] Of particular interest in this series are the products **1–4** obtained through addition of two alkynes onto the cyclopalladated complexes and where polysubstituted butadienyl units η^3-bound to the Pd are present.

However, these organometallic species often display an unexpected high thermal stability so that their depalladation to recover the organic fragment is only seldom achievable. The previous ways used to this purpose were to activate the organometallics by simple ligand changes on the Pd atom (changing Cl for I or using the cationic derivatives) or by treating them with an excess of maleic anhydride or pyridine at high temperatures.[2,3c,d,4] The efficiency of these processes proved to be very much dependent upon the nature of the starting materials. There is thus still an obvious need for finding more general ways inducing clean depalladation reactions.

Among these reactions, those observed with compounds having only phenyl substituents on the butadienyl fragment are of particular interest: since it was shown that they led to annelation reactions of phenyl groups.[1d,3] We have observed recently that this latter carbocyclization could be achieved in a rather efficient way (reaction conditions, yield and selectivity) by treating the organopalladium complexes with 4 equiv of triphenylphosphine in methanol.[3d] Consequently, we decided to apply this procedure to a larger set of such compounds and we used the following methodology: the new depalladation reaction was first performed on starting materials which were already depalladated by other routes in order to check whether the nature of the resulting compound was dependent upon the demetalating methods and also to compare the effectiveness of the new reaction. In a second step this procedure was then applied on a larger set of complexes some of which we were previously unable to demetalate.

Results and Discussion

It was established earlier that compound **1a** in refluxing chlorobenzene led mainly to its η^3-pentadienyl isomer **5** via a 1,3-H shift together with a heterocyclic cation, **6a**, in very low yield (eq 1).[4]

We have now found that the treatment of **1a** with PPh_3 in refluxing methanol (throughout the paper this procedure will be referred to as the phosphine-induced depalladation conditions) afforded selectively the cationic heterocycle **6b** in fairly good yield. The identity of **6b** was unambiguously established by analyzing the ^1H NMR spectrum of its BF_4 derivative which compares exactly with that of an authentic sample.[4] It appears from this new way of synthesis of the heterocyclic cation that another reaction

(1) (a) Bahsoun, A.; Dehand, J.; Pfeffer, M.; Zinsius, M.; Bouaoud, S. E.; LeBorgne, G. *J. Chem. Soc., Dalton Trans.* **1979**, 547. (b) Arlen, C.; Pfeffer, M.; Bars, O.; Grandjean, D. *J. Chem. Soc., Dalton Trans.* **1983**, 1535. (c) Dupont, J.; Pfeffer, M.; Daran, J. C.; Gouteron, J. *J. Chem. Soc., Dalton Trans.* **1988**, 2421. (d) Tao, W.; Silverberg, L. J.; Rheingold, A. L.; Heck, R. F. *Organometallics* **1989**, *8*, 2550. (e) Albert, J.; Granell, J.; Sales, J. *J. Organomet. Chem.* **1989**, *379*, 177.

(2) (a) Pfeffer, M. *Recl. Trav. Chim. Pays-Bas* **1990**, *109*, 567. (b) Wu, G.; Geib, S. J.; Rheingold, A. L.; Heck, R. F. *J. Org. Chem.* **1988**, *53*, 3238. (c) Wu, G.; Rheingold, A. L.; Heck, R. F. *Organometallics* **1987**, *6*, 2386.

(3) (a) Wu, G.; Rheingold, A. L.; Geib, S. J.; Heck, R. F. *Organometallics* **1987**, *6*, 1941. (b) Pfeffer, M.; Rotteveel, M. A.; Sutter, J. P.; DeCian, A.; Fischer, J. *J. Organomet. Chem.* **1989**, *371*, C21. (c) Pfeffer, M.; Rotteveel, M. A.; DeCian, A.; Fischer, J.; LeBorgne, G. *J. Organomet. Chem.* **1991**, *413*, C15. (d) Pfeffer, M.; Sutter, J. P.; Rotteveel, M. A.; DeCian, A.; Fischer, J. *Tetrahedron* **1992**, *48*, 2427.

(4) Maassarani, F.; Pfeffer, M.; LeBorgne, G. *Organometallics* **1987**, *6*, 2029.

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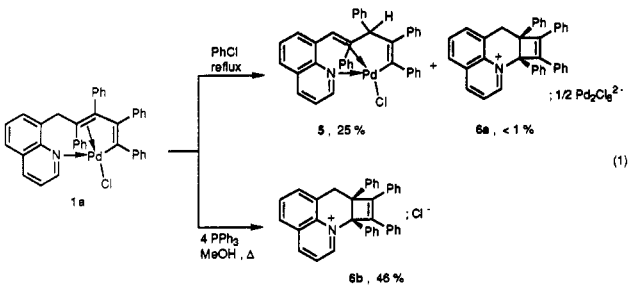
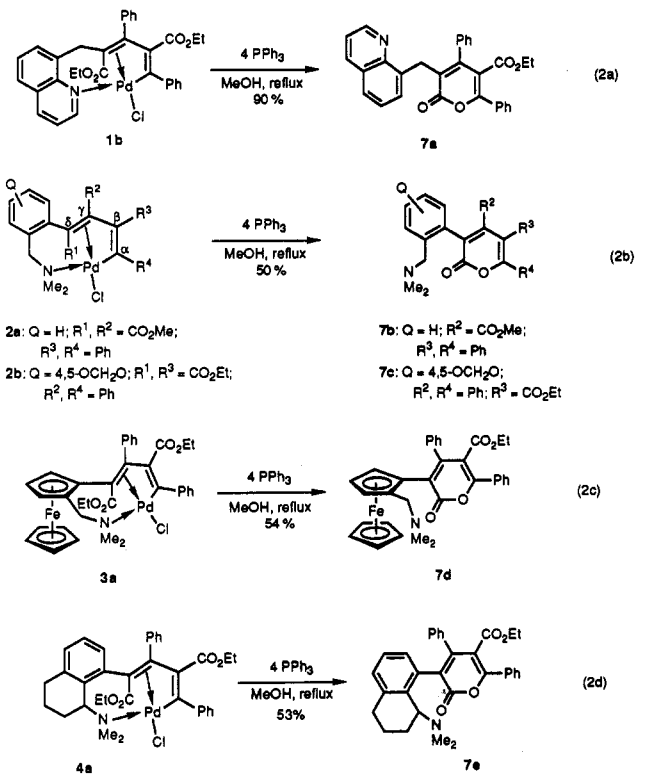


pathway for its formation can be proposed (Scheme I) which is actually much more likely than the one we proposed earlier. It involves at an early stage the decoordination of the nitrogen atom followed by its intramolecular addition on the η^2-bound olefin unit. The C–C bond of the cyclobutene ring is finally obtained via a classical reductive elimination process.

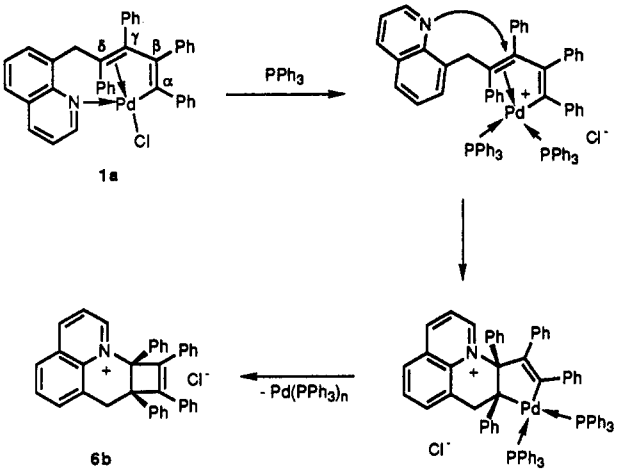
The demetalation of **1b**, after treatment with $AgBF_4$, was shown to afford the α-pyrone derivative **7a** in good yield, and a related result was observed when **2a** was treated with maleic anhydride in refluxing chlorobenzene affording **7b**.[3c] We now checked (eqs 2a and 2b) that the same



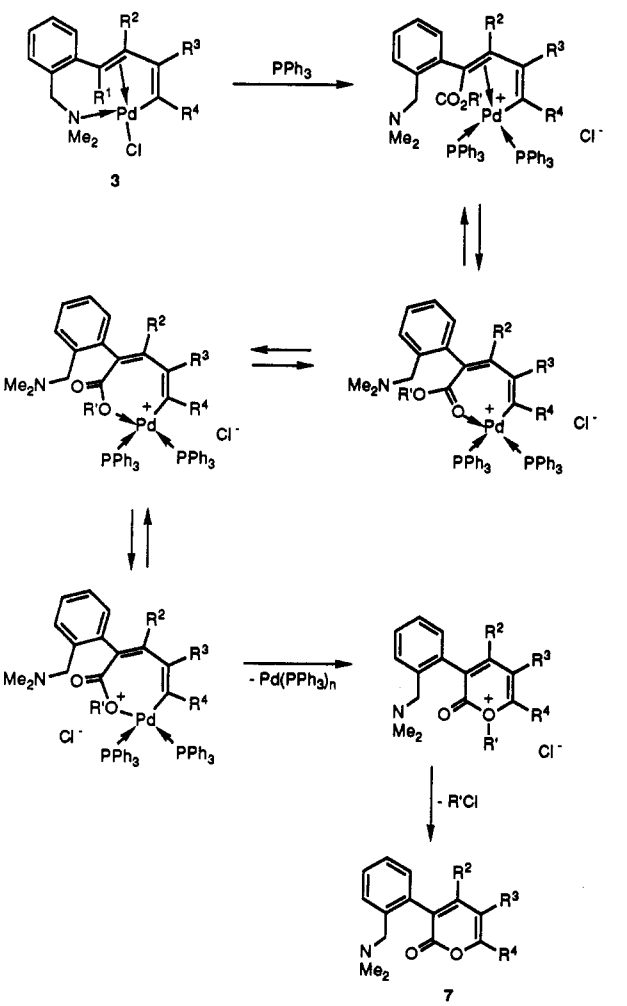
products **7a** and **7b** could be obtained when the starting complexes **1b** and **2a**, respectively, were treated under the novel depalladation conditions. It was possible to extend this synthesis to a larger variety of α-pyrones by varying the nature of the starting compounds (see eqs 2c and 2d).

We have so far no decisive evidence for rationalizing the formation of the O–C bond from the cationic intermediate. We might speculate however that a reasonable pathway would involve the decoordination of the N atom in the presence of triphenylphosphine (see Scheme II). The activation of the ester unit by Pd can then take place to form a seven-membered ring from which reductive elimination would afford the pyrone. Recently, Heck et al.[1d] have rationalized the synthesis of 3,4-diphenylisocoumarin by a related route.

Scheme I



Scheme II



It appears therefore from these initial results that the role played by PPh_3 in these reactions is likely to involve the modification of the linkage of the organic ligands around the Pd atom. Thus, at least two phosphines could coordinate to Pd by displacing both the chlorine and the nitrogen atoms, leading to a cationic species. This could dramatically decrease the chelate effect and at the same time increase the electrophilicity of the organo–Pd fragment, which is now more prone to intramolecular rearrangement. The phosphine effect in these reactions should be analogous to what was observed in the reactivity of palladium allyl units for which the addition of phosphine

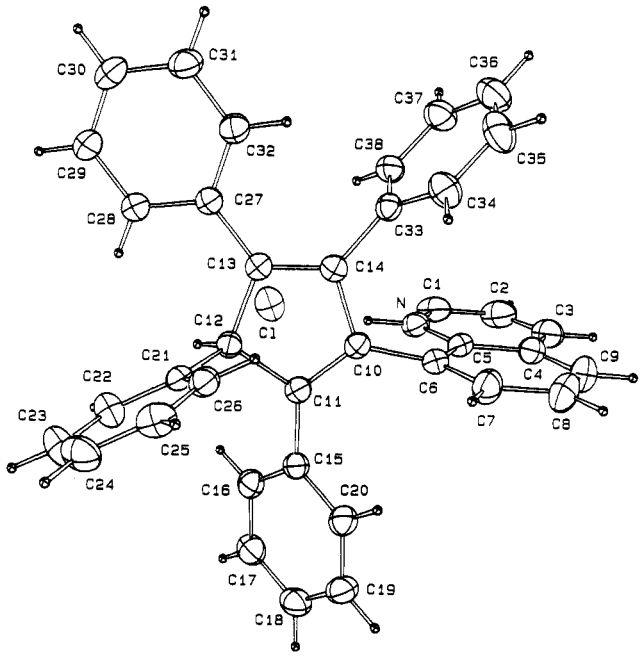
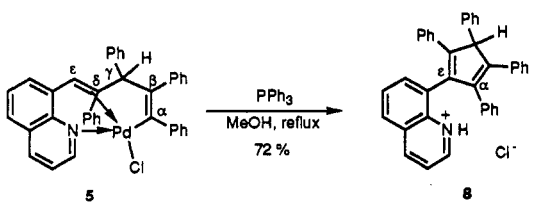


Figure 1. ORTEP plot of 8 showing the numbering scheme used. Ellipsoids are scaled to enclose 50% of the electronic density.

is well-known to increase dramatically the ease of the nucleophilic addition on the coordinated allyl fragment.

We have thus established through a series of reactions that the phosphine-induced depalladation conditions can be efficiently used for several organopalladium complexes since the nature of the organic products are the same as those obtained by other routes (see eqs 1, 2a, and 2b).

Previous attempts made to demetalate the η^3-pentadienyl complex **5** failed. This compound proved indeed to be stable toward thermolysis in refluxing chlorobenzene; moreover using the cationic derivatives of **5** (obtained in the presence of a silver salt) or performing this thermolysis in the presence of maleic anhydride did not lead to clean products. We have now found that the palladium atom can be easily and quantitatively removed from **5** using our phosphine-induced depalladation reaction. This afforded a new organic compound **8**.

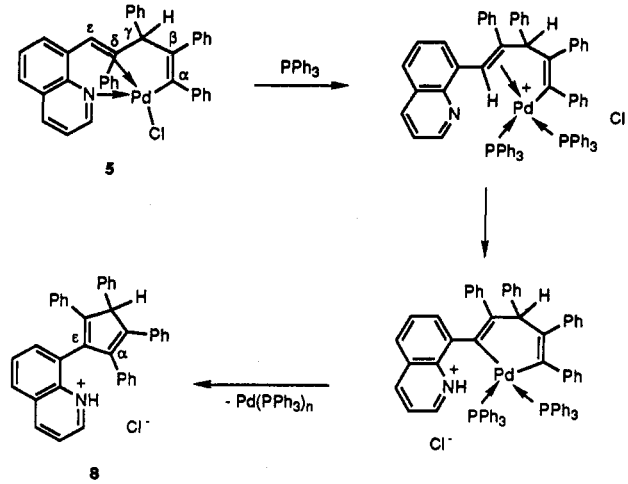


(3)

Microanalysis and mass spectra indicated that **8** was an isomer of the heterocyclic compound **6**, whereas the ^{1}H NMR spectrum showed that one proton signal was missing compared with the spectrum of **5**. The molecular structure of **8** was established through an X-ray diffraction study. An ORTEP diagram of the molecule is represented in Figure 1. It shows that **8** is a cyclopentadiene unit substituted by four phenyl and a protonated quinolinium group. The departure of the palladium atoms has thus resulted in the formation of a C–C bond, i.e. C14–C10; the hydrogen atom that was at C10 in the starting complex **5** is now at the nitrogen atom of the quinolinium unit in **8**.

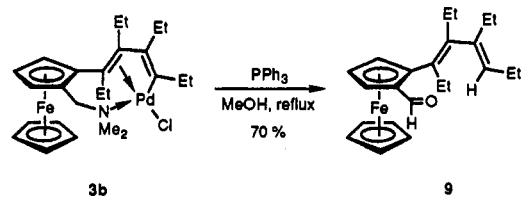
A likely reaction path that could rationalize the formation of **8** is depicted in Scheme III. Thus, a C–H

Scheme III



activation assisted by the presence of the intramolecular quinoline base on the olefin unit η^2-bound to Pd could lead to a palladacyclohexadienyl unit which precedes the C–C bond formation that leads to **8**. However we do not have at present definite arguments that could exclude other palladium-mediated pathways such as those we have encountered recently in related carbocyclization reactions.[3d]

We have previously shown that the depalladation reactions of **3b** could not be easily achieved; we observed instead several rearrangements of the molecule leading to novel η^3-allylic–Pd species via 1,4- or 1,5-H shifts. This H migration occurred from CH_2 groups of the ethyl substituents at either γ or δ positions with respect to Pd to the carbon that is σ-bonded to Pd (in the α position). However, when this reaction was performed in neat pyridine, we obtained the "Pd-free" ligand via protonolysis of the Pd–C bond of **3b**.[5] Applying the phosphine-induced depalladation conditions to **3b** afforded good yields (70%) of **9**. ^{1}H and ^{13}C NMR as well as mass spectra allowed us to assign to **9** the structure depicted in eq 4.

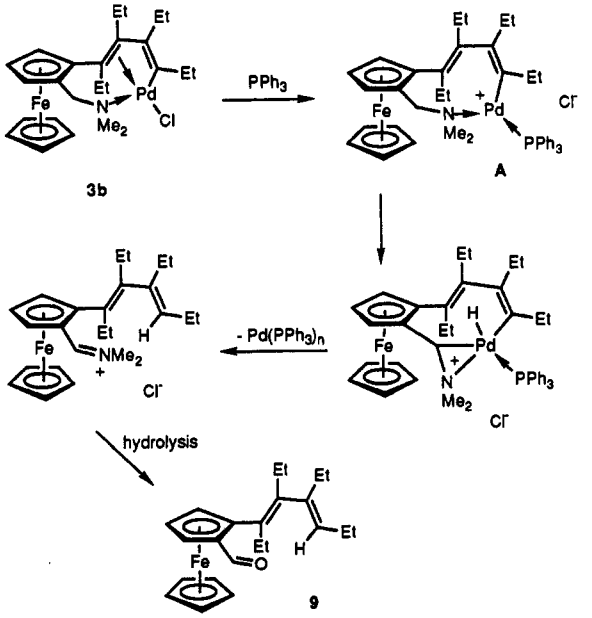


(4)

The formation of **9** is puzzling in that we observe now the replacement of the amine group by an aldehyde function on the ferrocenyl unit. Performing the same reaction in CD_3OD afforded the same compound **9** containing no deuterium atom. Thus the aldehyde and the vinylic protons cannot come from the solvent of the reaction, and therefore, they must come from the ferrocenyl ligand itself. A rather speculative reaction path is presented in Scheme IV. It involves at an early stage a C—H activation on the nitrogen methylene unit to afford an iminium ion. It is remarkable that this C—H activation occurs now specifically at the CH_2—N unit and not at any of the ethyl substituents, as was observed when this reaction was performed in the absence of PPh_3.[5] It might thus be that the trans influence of this latter ligand in the key intermediate A of Scheme IV is such that the C=C

(5) Sutter, J. P.; Pfeffer, M.; DeCian, A.; Fischer, J. *Organometallics* **1992**, *11*, 386.

Scheme IV



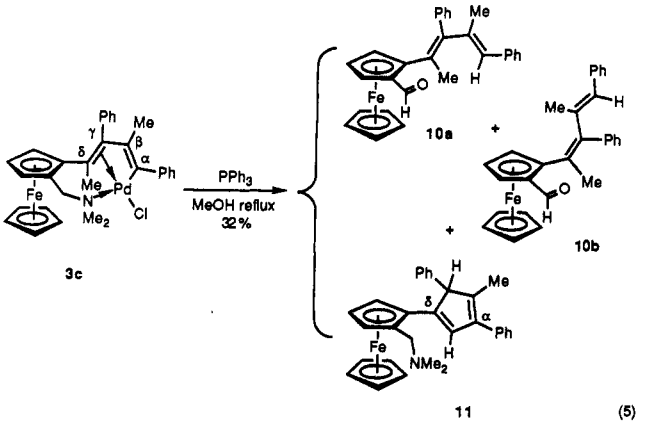
double bond trans to it is no longer η^2-coordinated to Pd and hence no C—H activation can take place at any of these ethyl groups. Such metalations at a carbon α to a nitrogen atom have been reported previously in other complexes.[6] The formation of the final compound **9** could then be rationalized by assuming that the iminium salt is hydrolyzed by traces of water present in the reaction mixture. Indeed, we checked that **9** was already present before any workup of the reaction product; thus the hydrolysis could not take place on the alumina column.

We, and others, have shown that the depalladation of the butadienyl units substituted by four phenyl groups could lead to annulation of the phenyl on the carbon γ or δ to the Pd,[1d,3] whereas the related system with four ethyl substituents did not result in C–C bond formation. In this latter case the Pd–C bond is usually cleaved as the result of intramolecular H shifts.[5]

In order to evaluate more precisely the role of the different substituents on the butadienyl chain during the departure of Pd we have now studied the depalladation of complex **3c** which was formed as a single isomer through insertion of 2 equiv of 1-phenylpropyne into the Pd–C bond of the cyclometalated [(*N*,*N*-dimethylamino)methyl]-ferrocene ligand. The structure of **3c** is deduced from previous results in this field which indicate that the preferred orientation of the substituents in the insertion product **3c** is as proposed.[1a] This will moreover be confirmed by the analysis of the depalladation products (see later).

The phosphine-induced depalladation of **3c** afforded low yields (30% after workup) of three products **10a**, **10b**, and **11** in a 4/1/5 ratio.

Compounds **10a** and **10b** could not be separated from each other and are likely to be two isomers since their ^{1}H NMR spectra are closely related. As for **9** the spectroscopic data for **10** suggest that an aldehyde function has sub-



(5)

stituted the CH_2NMe_2 unit whilst a vinylic proton is found at the carbon that was σ-bonded to Pd in **3c**. We suggest that the minor isomer **10b** is the result of a trans–cis isomerization around the C_γ=C_δ olefin unit. Such an isomerization has been described by Maitlis et al. in related palladium complexes, and it was suggested to occur via a metallocyclic flip process.[7] A related rearrangement has been observed more recently, as Heck et al. described the annulation of cyclopalladated *N*,*N*-dimethylbenzylamine with 3-hexyne.[1d]

The structure of **11** was mainly deduced from its ^{1}H NMR spectrum. It showed the presence of only one methyl group of the former butadienyl chain, together with two singlets at ca 5 ppm, each of them corresponding to one proton. We propose that, as for **8**, a cyclopentadiene ring has been formed. It is thus apparent that this depalladation procedure is much less selective than the one we observed for compound **3b**. One reason for this nonselectivity could be different steric effects of ethyl versus methyl or phenyl groups. These latter might well be less sterically demanding so that some kind of interaction with Pd could still take place. The formation of the aldehyde-containing compounds **10a** and **10b** can follow the same pathway as **9**. However, the formation of the five-membered carbocycle in **11** is likely to be the result of (i) a 1,3-H shift of the methyl adjacent to the ferrocene unit (see the discussion on this point below) followed (ii) by a second C–H activation which leads to a six-membered palladacycle whose reductive elimination affords compound **11**.

We have shown that for **3b** 1,4- or 1,5-H shifts were observed,[5] this resulting invariably in the cleavage of the Pd–C bond. However, we have also demonstrated in this paper that the formation of **8** could only be rationalized by assuming that a 1,3-H shift takes place prior to the depalladation and subsequent cyclization of **5**. It appears therefore that the H migrations along the butadienyl units may follow different routes, the nature of the resulting compound being mainly dependent upon the basicity of the palladated carbon atom. If this latter bears an ethyl group, this results selectively in the cleavage of the Pd–C bond, whereas if it bears a phenyl unit, a more classical isomerization of an olefin substituted by an alkyl group (1,3-H shift) could be observed.

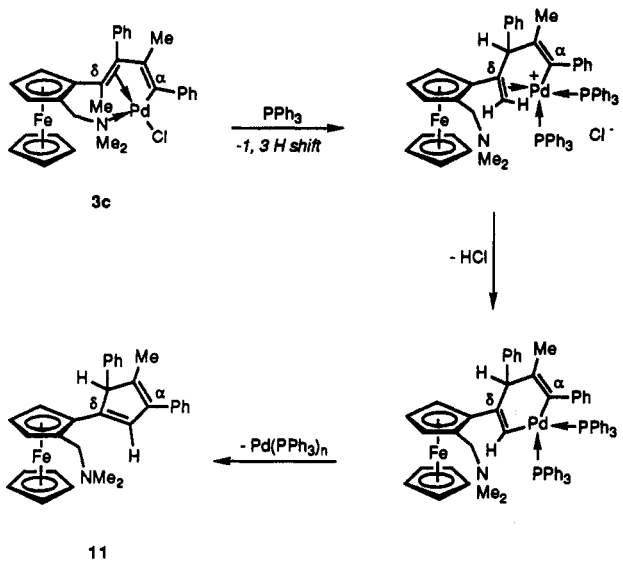
Conclusion

These new demetalation procedures applied to organopalladium compounds presented in this study proved to be more efficient than previous methods used in our

(6) Booij, M.; Kiers, N. H.; Meetsma, A.; Teuben, J. H.; Smeets, W. J. J.; Spek, A. *Organometallics* **1989**, *8*, 2454. Abbenhuis, H. C. L.; Grove, D. M.; Van Mier, G. P. M.; Spek, A. L.; Van Koten, G. *Recl. Trav. Chim. Pays-Bas* **1990**, *109*, 361. Dupont, J.; Beydoun, N.; Pfeffer, M. *J. Chem. Soc, Dalton Trans* **1989**, 1715. Grinter, T. J.; Leaver, D.; O'Neil, R. M. *Inorg. Nucl. Chem. Lett.* **1980**, *16*, 145. Castan, P.; Jaud, J.; Johnson, N. P.; Soules, R. *J. Am. Chem. Soc.* **1985**, *107*, 5011. See also ref 11 for a related palladium-mediated rearrangement that involves a N–CH_3 group.

(7) Maitlis, P. M. *J. Organomet. Chem.* **1980**, *200*, 161.

Scheme V



laboratory. They take place under rather mild conditions and afford good yields of the resulting organic compounds even in the cases where the previous methods were not operative. The main conclusions that can be inferred from the present and earlier work is that the depalladation of polysubstituted butadienyl fragments is selective in that the nature of the organic product obtained depends only upon the nature of the substituents.

Experimental Section

General Considerations. All reactions were performed by using standard Schlenk tube and vacuum line techniques. All solvents used were dried and distilled under N_2 prior to use. Chromatographic separations of the products were achieved on Al_2O_3 90, Activity II–III, 70–230 mesh, or on silica gel (Kieselgel 60), 70–230 mesh (Merck). ^1H and proton-decoupled ^{13}C NMR spectra ($CDCl_3$, 239 K, δ in ppm, J in Hz) were recorded at 200.1 and 50.3 MHz), respectively, on a Bruker SY 200 instrument, using $SiMe_4$ as reference. Commercial compounds were used as received. Compounds **1a**,[4] **2a**,[4] **3b**,[5] and **5**[4] as well as the cyclopalladated 8-methylquinoline,[8] [(*N*,*N*-dimethylamino)-methyl]-4,5-dioxymethylenebenzene,[9] [(*N*,*N*-dimethylamino)-methyl]ferrocene,[10] and 1,2,3,4-tetrahydro-1-(*N*,*N*-dimethylamino)naphthalene[11] ligands were prepared according to published methods.

Synthesis. Compound 1b (Optimization of the Published Method).[4] A suspension of cyclopalladated 8-methylquinoline chloro dimer (1.14 g, 2 mmol) and ethyl 3-phenylpropynoate (1.66 mL, 10 mmol), in CH_2Cl_2 (30 mL) was refluxed for 15 h. The obtained orange solution was filtered on Celite (2.5 × 5-cm column) and concentrated to ca. 10 mL. Addition of hexane gave an orange precipitate of **1b** (2.37 g, 92%). The analytical data were as previously reported.[12]

Compounds 2b and 2c. A suspension of the palladated [(*N*,*N*-dimethylamino)methyl]-4,5-dioxymethylenebenzene (640 mg, 1 mmol) and ethyl 3-phenylpropylnoate (0.7 mL, 4.2 mmol) in CH_2Cl_2 (30 mL) was stirred at room temperature for 8 h. Concentration of the obtained solution in vacuo and addition of hexane gave a yellow precipitate of **2b** and **2c** in a 2/1 ratio. The two isomers were separated by chromatography on alumina (16- × 2.5-cm column, CH_2Cl_2). Compound **2b** was obtained by elution with CH_2Cl_2 whereas **2c** was eluted with pure acetone.

^1H NMR: **2b** δ = 7.55–7.20 (m, 10 H, Ar), 7.10 and 6.41 (2s, 2 H, C_6H_2), 6.10 and 6.07 (2s, 2 H, CH_2O_2), 4.32 (q, 2 H, CH_2CH_3, $^3J_{HH}$ = 7.15), 3.84 (m, 2 H, CH_2CH_3), 2.71 and 2.54 (2d, 2 H, CH_2N, $^2J_{HH}$ = 13.5), 2.64 and 2.24 (2s, 6 H, NMe_2), 1.24 and 0.81 (2t, 6 H, CH_2CH_3, $^3J_{HH}$ = 7.2 and 7.15); **2c** δ = 7.50–7.12 (m, 11 H, Ar), 6.44 (s, 1 H, C_6H_2), 6.12 and 6.09 (2s, 2 H, CH_2O_2), 4.30 (m, 4 H, CH_2CH_3), 2.69 and 2.28 (2s, 6 H, NMe_2), 2.63 (2d, 2 H, CH_2N), 1.33 and 1.20 (2t, 6 H, CH_2CH_3, $^3J_{HH}$ = 7.15 and 7.10).

Compound 3a. A solution of ethyl 3-phenylpropynoate (0.35 mL, 2.1 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a solution of the palladated [(*N*,*N*-dimethylamino)methyl]ferrocene (384 mg, 0.5 mmol) in CH_2Cl_2 (15 mL). The reaction mixture was stirred at room temperature for 3 h, and the solvent was removed in vacuo. The residue was washed with Et_2O, dissolved in 5 mL of CH_2Cl_2, and **3a** (620 mg, 86%) was precipitated as a yellow solid by addition of hexane.

Anal. Calcd for $C_{34}H_{36}NO_4ClFePd$: C, 56.68; H, 5.00; N, 1.91. Found: C, 56.27; H, 5.05; N, 1.84. ^1H NMR: δ = 7.55, 7.32, and 7.21 (3m, 10 H, Ar), 4.79, 4.37, and 4.00 (3m, 3 H, C_5H_3), 4.31 (s, C_5H_5), 3.00 and 2.38 (2s, 6 H, NMe_2), 2.45 and 1.84 (2d, 2 H, CH_2N, $^2J_{HH}$ = 14.1), 4.32 and 3.85 (2q, 4 H, CH_2CH_3), 1.27 and 0.86 (2t, 6 H, CH_2CH_3, $^3J_{HH}$ = 7.1).

Compound 3c. A solution of 1-phenylpropyne (0.25 mL, 2 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a solution of the palladated [(*N*,*N*-dimethylamino)methyl]ferrocene (384 mg, 0.5 mmol) in CH_2Cl_2 (30 mL). The reaction mixture was stirred at room temperature for 3 h and the solvent removed in vacuo. The residue was washed with pentane, dissolved in CH_2Cl_2 (3–5 mL) and chromatographed on silica gel (6 × 2.5 cm column, CH_2Cl_2). **3c** (430 mg, 70%) was obtained from the first fraction as an orange solid by removing the solvent in vacuo. **3c** can be crystallized from a CH_2Cl_2–Et_2O solution layered with hexane.

Anal. Calcd for $C_{30}H_{32}NClFePd + {}^1/_2CH_2Cl_2$: C, 56.63; H, 5.11; N, 1.99. Found: C, 56.33; H, 4.99; N, 1.99. ^1H NMR: δ = 7.53–7.14 (m, 10 H, Ar), 4.70, 4.30, and 3.88 (3m, 3 H, C_5H_3), 4.32 (s, 5 H, C_5H_5), 2.93 and 2.47 (2s, 6 H, 2 CH_3), 2.21 and 1.77 (2d, 2 H, CH_2N, $^2J_{HH}$ = 14.4).

Compounds 4a and 4b. A suspension of {[Pd(PhC=C(CO_2Et)–$C_{10}H_{10}NMe_2$)(μ-Cl)]$_2$} (compound **3** of ref 11) (664 mg, 0.5 mmol) and ethyl 3-phenylpropynoate (0.17 mL, 1 mmol) in chlorobenzene (15 mL) was heated at 80 °C for 30 min. The solvent of the obtained yellow solution was concentrated to dryness and the residue dissolved in CH_2Cl_2 (5 mL). Addition of hexane gave a yellow precipitate of **4a** and **5b** in a 3/2 ratio. The two isomers were separated by chromatography on alumina (16- × 2.5-cm column, CH_2Cl_2). Compound **4a** was obtained by elution with a CH_2Cl_2–acetone (99/1) solution, and the elution with pure acetone afforded **4b**.

An analytically pure sample of a mixture of **4a** and **4b** was obtained by crystallization from a CH_2Cl_2–hexane solution.

Anal. Calcd for $C_{34}H_{36}NO_4ClPd + {}^1/_4C_6H_{14}$: C, 62.01; H, 5.74; N, 2.05. Found: C, 62.06; H, 5.73; N, 2.04. ^1H NMR: **4a** δ = 7.51 (d, 1 H, Ar, $^3J_{HH}$ = 7.9), 7.36–7.26 (m, 11 H, Ar), 7.17 (d, 1 H, Ar, $^3J_{HH}$ = 7.5), 4.37 (q, 2 H, CH_2CH_3), 3.80 (m, 2 H, CH_2CH_3), 3.04 (m, 1 H, CHN), 2.88 and 2.16 (2s, 6 H, NMe_2), 2.62, 1.73–0.73 (m, 6 H, CH_2), 1.26 and 0.77 (2t, 6 H, CH_2CH_3, $^3J_{HH}$ = 7.15 and 7.10); **4b** δ = 7.64 (d, 1 H, Ar, $^3J_{HH}$ = 6.06), 7.40–7.05 (m, 12 H, Ar), 4.35 (m, 4 H, CH_2CH_3), 2.92 and 2.19 (2s, 6 H, NMe_2), 3.03–0.73 (5m, 7 H, CHN and CH_2), 1.33 and 1.21 (2t, 6 H, CH_2CH_3, $^3J_{HH}$ = 7.10).

Compound 6b. A suspension of **1a** (640 mg, 1 mmol) and PPh_3 (1.50 g, 4 mmol) in methanol (20 mL) was refluxed for 1 h. After cooling, the yellow precipitate of $Pd(PPh_3)_n$ was removed by filtration and the filtrate dried in vacuo. The residue was extracted with methanol (10–15 mL), the extract was filtered, and the residue was again dried in vacuo. Dissolving the obtained solid in CH_2Cl_2 (10 mL) followed by addition of Et_2O (30 mL) and hexane (30 mL) afforded **6** as a light yellow solid. Analytical

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pure **6b** (245 mg, 46%) was obtained by crystallization from a CH_2Cl_2 solution layered with Et_2O.

Anal. Calcd for $C_{38}H_{28}NCl$: C, 85.45; H, 5.28; N, 2.62. Found: C, 85.01; H, 5.10; N, 2.06. ^1H NMR: δ = 9.86 (d, 1 H, Ar, $^3J_{HH}$ = 7.45), 8.68 (d, 2 H, Ar, $^3J_{HH}$ = 6.2), 8.12 (m, 1 H, Ar), 7.91 (m, 2 H, Ar), 7.44–7.05 (m, 18 H, Ar), 6.70 (d, 2 H, Ar, $^3J_{HH}$ = 8.0), 4.69 and 4.10 (2d, 2 H, CH_2, $^2J_{HH}$ = 16.1).

Compound 7a. A suspension of **1b** (642 mg, 1 mmol) and PPh_3 (1.05 g, 4 mmol) in MeOH (30 mL) was refluxed for 2.5 h. After cooling, the suspension was filtered and the filtrate dried in vacuo. The residue was extracted with CH_2Cl_2 (3–5 mL) and chromatographed on alumina (15- × 2.5-cm column, hexane–Et_2O (9/1)). Elution with hexane–Et_2O (9/1) afforded a first fraction containing the excess PPh_3. Elution with pure CH_2Cl_2 gave the pyrone **7a** (425 mg, 90%) which was recovered as a white solid after addition of hexane to a concentrated solution in CH_2Cl_2.

IR (KBr pellet): ν_{CO} = 1716 cm^{-1}. The NMR data were as previously reported.[3c]

Compound 7b. A suspension of **2a** (596 mg, 1 mmol) and PPh_3 (1.05 g, 4 mmol) in MeOH (25 mL) was refluxed for 2.5 h. After cooling, the suspension was filtered and the filtrate dried in vacuo. The residue was extracted with Et_2O (2 × 10 mL) and the extract concentrated to 5 mL and chromatographed on alumina (12- × 2.5-cm column, pentane–Et_2O (9/1)). Elution with pentane–Et_2O (9/1) afforded a fraction containing the excess PPh_3. Further elution with pure Et_2O gave a light orange solution yielding **7b** (220 mg, 50%) as a pale orange oil after solvent removal.

Anal. Calcd for $C_{28}H_{25}NO_4$: C, 76.52; H, 5.73; N, 3.19. Found: C, 77.20; H, 5.85; N, 3.20. ^1H NMR: δ = 7.47–7.18 (m, 14 H, Ar), 3.60 and 3.40 (2d, 2 H, CH_2N, $^2J_{HH}$ = 14.0), 3.19 (s, 3 H, OCH_3), 2.21 (s, 6 H, NMe_2). Mass spectra: m/z = 439 (M^+), 411 (–CO), 396 (–COMe), 394, 352. IR (film): ν_{CO} = 1728 cm^{-1}.

Compound 7c. The same procedure as that used for **7b** yielded **7c** (50%) as a light yellow solid.

^1H NMR: δ = 7.75 (m, 10 H, Ar), 6.90 and 6.48 (2s, 2 H, C_6H_2), 5.90 and 5.87 (2s, 2 H, CH_2O_2), 3.84 (q, 2 H, CH_2CH_3, $^3J_{HH}$ = 7.1), 3.23 and 3.01 (2d, 2 H, CH_2N, $^2J_{HH}$ = 13.5), 2.16 (s, 6 H, NMe_2), 0.83 (t, 3 H, CH_2CH_3). ^{13}C NMR: δ = 165.9, 160.7, 158.6, 151.4, 147.8, 146.1, 135.5, 132.8, 131.8, 131.0, 128.6, 128.5, 128.0, 127.9, 125.6, 124.9, 114.8 (Ar and =C), 110.9 and 109.0 (CH, C_6H_2), 101.0 (CH_2O_2), 61.7 and 61.6 (CH_2), 13.3 (CH_3). Mass spectra: m/z = 497 (M^+), 452 (–OEt).

Compound 7d. The same procedure as that used for **7b** yielded **7d** (54%) as a purple waxy material. A solid form was obtained from a saturated hexane solution at –30 °C.

Anal. Calcd for $C_{33}H_{31}NO_4Fe$: C, 70.6; H, 5.5; N, 2.5. Found: C, 69.6; H, 6.1; N, 2.5. ^1H NMR: δ = 7.75–7.20 (m, 10 H, Ar), 4.26 and 3.37 (2m, 2 H, C_5H_3), 4.15 (s, 5 H, C_5H_5), 3.80 (m, 4 H, CH_2CH_3 + C_5H_3 + CH_2N), 3.10 (d, 1 H, CH_2N, $^2J_{HH}$ = 13.1), 2.16 (s, 6 H, NMe_2), 0.82 (t, 3 H, CH_2CH_3, $^3J_{HH}$ = 7.1). ^{13}C NMR: δ = 166.2, 159.4, 157.0, 152.1, 137.2, 132.0, 122.7, 115.3, 128.6–127.8 (Ar + =C), 87.4, 79.7, 71.6, 70.8, 65.7 (C_5H_3), 70.3 (C_5H_5), 61.1 and 58.8 (CH_2), 45.4 (NMe_2), 13.3 (CH_3). Mass spectra: m/z = 561 (M^+), 495 (–C_5H_6). IR (KBr pellet): ν_{CO} = 1730 cm^{-1}.

Compound 7e. A suspension of **4a** (165 mg, 0.25 mmol) and PPh_3(262 mg, 1 mmol) in MeOH (10 mL) was refluxed for 5 h. After cooling and filtration, the solvent was removed in vacuo. The residue was extracted with CH_2Cl_2 (3 mL) and chromatographed on alumina (10- × 2-cm column, hexane–CH_2Cl_2 (7/3)). Elution with hexane–CH_2Cl_2 (7/3) afforded a fraction containing the excess PPh_3. Further elution with pure CH_2Cl_2 gave a light yellow solution from which **7e** (65 mg, 53%) was obtained as a yellow wax after solvent removal.

^1H NMR: δ = 7.73–6.88 (m, 13 H, Ar), 4.11–0.80 (m, 7 H, C_4H_7), 4.07 (m, 2 H, CH_2CH_3), 2.09 (s, 6 H, NMe_2), 0.79 (t, 3 H, CH_2CH_3, $^3J_{HH}$ = 7.1). Mass spectra: m/z = 493 (M^+), 450 (–OEt). IR (KBr pellet): ν_{CO} = 1725 cm^{-1}.

Compound 8. A suspension of complex **5** (640 mg, 1 mmol) and PPh_3 (1.05 g, 4 mmol) in MeOH (20 mL) was refluxed for 1.5 h. After cooling and filtration, the solution was dried in vacuo. The residue was extracted with CH_2Cl_2 (5 mL), and **8** (383 mg, 72%) was obtained as a yellow solid by addition of Et_2O. Analytically pure **8** was crystallized from a MeOH solution layered with Et_2O.

Table I. Crystal Parameters and Experimental Details for Compound 8

formula	$C_{38}H_{28}NCl$
mol wt	534.4
color	yellow
cryst syst	triclinic
a (Å)	17.119(5)
b (Å)	10.635(3)
c (Å)	8.739(3)
α (deg)	113.92(2)
β (deg)	96.14(2)
γ (deg)	99.02(2)
vol (Å^3)	1410.5
Z	2
D_{calc} (g·cm^{-3})	1.257
wavelength (Å)	1.5418
μ (cm^{-1})	13.910
space group	$P\bar{1}$
cryst dimens (mm)	0.18 × 0.22 × 0.36
temp (°C)	–100
radiation	graphite monochromated Cu Kα
mode	$\theta/2\theta$ flying step scan
scan speed (deg^{-1})	0.020
step width (deg)	0.03
scan width (deg)	0.80 + 0.14 tan(θ)
octants	$\pm h,\pm k,+l$
θ min/max (deg)	3/55
no. of data collected	3370
no. of data with $I > 3\sigma(I)$	0.88/1.09
$R(F)$	0.034
$R_w(F)$	0.059
GOF	1.358

Anal. Calcd for $C_{38}H_{28}NCl$: C, 85.45; H, 5.28; N, 2.62. Found: C, 85.37; H, 5.27; N, 2.63. ^1H NMR: δ = 9.15 (m, 1 H, Ar), 6.80 (d, 1 H, Ar, $^3J_{HH}$ = 8.0), 8.18 (d, 1 H, Ar, $^3J_{HH}$ = 6.9), 7.82 (m, 2 H, Ar), 7.63 (m, 1 H, Ar), 7.25–6.73 (m, 20 H, Ar + NH), 6.07 (s, 1 H, CH). Mass spectra: m/z = 498 (M^+), 497 (–H), 496 (–2H).

Compound 9. A suspension of **3b** (548 mg, 1 mmol) and PPh_3 (1.05 g, 4 mmol) in MeOH (20 mL) was refluxed for 1 h. After cooling and filtration, the solution was dried in vacuo. The residue was extracted with Et_2O and chromatographed on alumina (15 × 2.5-cm column, hexane). Elution with hexane–CH_2Cl_2 (9/1) afforded a fraction containing the excess PPh_3. Further elution with hexane–CH_2Cl_2 (1/1) gave a yellow solution yielding **9** (265 mg, 70%) by evaporation of the solvent.

^1H NMR: δ = 9.74 (s, 1 H, CHO), 4.94 (t, 1 H, CHEt, $^3J_{HH}$ = 7.2), 4.79, 4.60, and 4.33 (3m, 3 H, C_5H_3), 4.22 (s, 5 H, C_5H_5), 2.70, 2.30, 1.80, and 1.41 (4m, 8 H, CH_2CH_3), 1.28, 0.97, 0.78, and 0.73 (4t, 12 H, CH_2CH_3, $^3J_{HH}$ = 7.5). ^{13}C NMR: δ 192.7 (CO), 148.3, 140.5 and 127.2 (C=C), 132.8 (=CH), 98.1, 77.8, 73.1, 71.1, 65.4 (C_5H_3), 70.3 (C_5H_5), 29.5, 26.4, 23.4, and 21.1 (CH_2), 15.3, 13.8, 13.4, and 13.3 (CH_3). Mass spectra: m/z = 378 (M^+), 349 (–CHO), 321. IR (KBr): ν_{CO} = 1677 cm^{-1}.

Compounds 10a, 10b, and 11. A suspension of **3c** (616 mg, 1 mmol) and PPh_3 (1.05 g, 4 mmol) in MeOH (15 mL) was refluxed for 30 min. After cooling and filtration, the solution was dried in vacuo. The residue was extracted with CH_2Cl_2 (2–3 mL) and chromatographed on alumina (15- × 2.5-cm column, hexane–Et_2O (9/1)). Elution with hexane–Et_2O (9/1) afforded a fraction containing PPh_3. Further elution with hexane–Et_2O (7/3) gave a yellow solution yielding **11** (70 mg, 15%) by solvent evaporation. Compounds **10a** and **10b** (4/1 ratio) were obtained from the fraction eluted with hexane–Et_2O (1/1) as an orange oil after solvent removal (70 mg, 16%).

^1H NMR: **10a** δ = 10.08 (s, 1 H, CHO), 7.42–7.11 (m, 8 H, Ar), 6.97 (d, 2 H, Ar, $^3J_{HH}$ = 7.5), 6.07 (s, 1 H, =CH), 4.88, 4.72, and 4.59 (3m, 3 H, C_5H_3), 4.32 (s, 5 H, C_5H_5), 2.21 and 1.57 (2s, 6 H, Me); **10b** δ = 9.63 (s, 1 H, CHO), 7.43–6.95 (m, 10 H, Ar), 6.61 (s, 1 H, =CH), 4.67, 4.60, and 3.76 (3m, 3 H, C_5H_3), 4.27 (s, 5 H, C_5H_5), 2.44 and 2.19 (2s, 6 H, Me); **11** δ = 7.69–7.25 (m, 10 H, Ar),

Table II. Positional Parameters and Their Esd's for Compound 8

atom	x	y	z	B^a (Å^2)
Cl	0.39920 (3)	0.26179 (5)	0.38298 (6)	4.32 (1)
N	0.4076 (1)	0.4572 (2)	0.7461 (2)	3.16 (4)
C1	0.4726 (1)	0.5498 (2)	0.7604 (3)	3.98 (5)
C2	0.5057 (1)	0.6638 (2)	0.9121 (3)	4.84 (6)
C3	0.4713 (2)	0.6826 (2)	1.0508 (3)	4.89 (6)
C4	0.4009 (1)	0.5844 (2)	1.0382 (2)	3.89 (5)
C5	0.3690 (1)	0.4681 (2)	0.8785 (2)	2.99 (4)
C6	0.2994 (1)	0.3657 (2)	0.8545 (2)	2.87 (4)
C7	0.2648 (1)	0.3813 (2)	0.9936 (2)	4.12 (5)
C8	0.2969 (2)	0.4971 (3)	1.1536 (3)	5.44 (7)
C9	0.3626 (2)	0.5955 (2)	1.1744 (3)	5.13 (7)
C10	0.2621 (1)	0.2564 (2)	0.6805 (2)	2.56 (4)
C11	0.2735 (1)	0.1249 (2)	0.5985 (2)	2.60 (4)
C12	0.2263 (1)	0.0610 (2)	0.4172 (2)	2.63 (4)
C13	0.1900 (1)	0.1795 (2)	0.4086 (2)	2.62 (4)
C14	0.2117 (1)	0.2926 (2)	0.5628 (2)	2.69 (4)
C15	0.3262 (1)	0.0525 (2)	0.6616 (2)	2.88 (4)
C16	0.3795 (1)	−0.0138 (2)	0.5642 (2)	3.37 (5)
C17	0.4327 (1)	−0.0760 (2)	0.6252 (3)	4.02 (5)
C18	0.4324 (1)	−0.0746 (2)	0.7831 (3)	4.32 (5)
C19	0.3793 (1)	−0.0109 (2)	0.8815 (2)	4.17 (5)
C20	0.3260 (1)	0.0526 (2)	0.8216 (2)	3.45 (5)
C21	0.1664 (1)	−0.0751 (2)	0.3769 (2)	2.64 (4)
C22	0.1756 (1)	−0.2037 (2)	0.2613 (3)	3.78 (5)
C23	0.1224 (1)	−0.3274 (2)	0.2313 (3)	4.70 (6)
C24	0.0606 (1)	−0.3231 (2)	0.3185 (3)	4.63 (6)
C25	0.0502 (1)	−0.1958 (2)	0.4352 (2)	3.87 (5)
C26	0.1030 (1)	−0.0728 (2)	0.4634 (2)	3.18 (5)
C27	0.1431 (1)	0.1686 (2)	0.2507 (2)	2.69 (4)
C28	0.1462 (1)	0.0614 (2)	0.0937 (2)	3.33 (5)
C29	0.1027 (1)	0.0499 (2)	−0.0568 (2)	3.89 (5)
C30	0.0568 (1)	0.1440 (2)	−0.0556 (2)	3.78 (5)
C31	0.0537 (1)	0.2506 (2)	0.0968 (2)	3.77 (5)
C32	0.0953 (1)	0.2629 (2)	0.2487 (2)	3.36 (5)
C33	0.2021 (1)	0.4394 (2)	0.6159 (2)	2.72 (4)
C34	0.1537 (1)	0.4977 (2)	0.7297 (3)	3.99 (5)
C35	0.1486 (1)	0.6376 (2)	0.7807 (3)	5.00 (6)
C36	0.1928 (1)	0.7191 (2)	0.7187 (3)	4.69 (6)
C37	0.2431 (1)	0.6637 (2)	0.6095 (3)	4.22 (5)
C38	0.2477 (1)	0.5256 (2)	0.5595 (2)	3.29 (5)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

5.0 and 4.98 (2s, 2 H, =CH), 4.13 and 3.98 (2m, 3 H, C_5H_3), 4.07 (s, 6 H, C_5H_5 and C_5H_3), 3.84 and 2.88 (2d, 2 H, CH_2N, $^2J_{HH}$ = 12.7), 2.16 (s, 6 H, NMe_2), 1.99 (s, 3 H, Me). Mass spectra: **10** m/z = 446 (M^+), 417 (−CHO); **11** m/z = 473 (M^+), 429 (−NMe_2). IR (film on KBr): **10** ν_{CO} = 1672 cm^{-1}.

Crystal Structure Determination of Compound 8. Suitable single crystals of **8** were obtained from a MeOH solution layered with Et_2O. A systematic search in reciprocal space using a Philips PW1100/16 automatic diffractometer showed that crystals of **8** belong to the triclinic system. Quantitative data were obtained at −100 °C achieved using a local-built gas flow device. All experimental parameters used are given in Table I. The resulting data set was transferred to a VAX computer, and for all subsequent calculations the Enraf-Nonius SDP/VAX package[13] was used with the exception of a local data reduction program. Three standard reflections measured every hour during the entire data collection period showed no significant trend. The raw step-scan data were converted to intensities using the Lehmann–Larsen method[14] and then corrected for Lorentz and polarization factors. The structure was solved using MULTAN.[15] After refinement of the heavy atom, a difference-Fourier map revealed maximas of residual electronic density close to the positions expected for hydrogen atoms; they were introduced in structure factor calculations by their computed coordinates (C–H = 0.95 Å) and isotopic temperature factors such as $B(H) = 1.3B_{eqv}$(C) Å^2 but not refined. No absorption corrections were applied since face indexation was not possible under the cold gas stream and in view of the small absorption coefficient (full least-squares refinements; $\sigma^2(F^2) = \sigma^2$ counts + $(pI)^2$). A final difference map revealed no significant maxima. The scattering factor coefficients and anomalous dispersion coefficients come respectively from ref 16.

Table III. Selected Bond Lengths (Å) and Angles (deg) for Compound 8

Interatomic Distances

C10–C11	1.346(3)	C13–C14	1.356(3)
C10–C14	1.478(3)	C12–C21	1.522(3)
C11–C12	1.519(3)	C6–C10	1.482(3)
C12–C13	1.513(3)		

Bond Angles

C11–C10–C14	110.2(2)	C12–C13–C14	109.0(2)
C10–C11–C12	108.4(2)	C10–C14–C13	108.8(2)
C11–C12–C13	103.5(2)	C11–C12–C21	111.5(2)

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Supplementary Material Available: Tables of bond distances and angles, H atom coordinates, and thermal parameters for **8** (6 pages). Ordering information is given on any current masthead page.

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(16) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, U.K., 1974; Vol. IV, (a) Table 2.2b, (b) Table 2.3.1.