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Metal-Assisted Synthesis of New and Highly Functionalized Diphosphines

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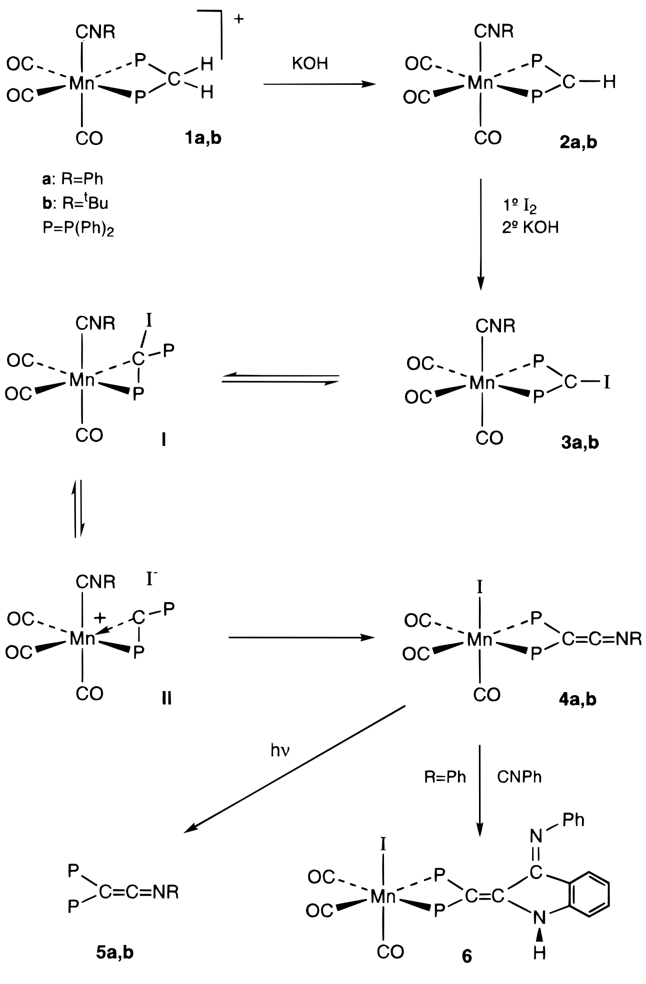
*Summary: The coupling of coordinated isocyanide with a fragment diphosphinocarbene in the complexes fac-[Mn(CO)$_3$(CNR){(PPh$_2$)$_2$CI}] (**3a**, R = Ph; **3b**, R = ^{t}Bu) leads to the formation of **4a,b**, which contain the new ketenimines [(PPh$_2$)$_2$C═C═NR] (**5a,b**). The N-phenylketenimine in **4a** undergoes a [4 + 1] cycloaddition by treatment with phenyl isocyanide to give **6**, a neutral complex containing a unique 2-(diphosphinomethylidene)-3-imino-2,3-dihydroindole ligand.*

Scheme 1



Diphosphine ligands play a crucial role in coordination and organometallic chemistry, owing to their ability to stabilize a great variety of metal complexes in a number of oxidation states[1] as well as to their application in homogeneous catalysis.[2] Even more, the design of new transition-metal catalysts strongly depends on the availability of new types of diphosphines; notably, it has been shown that functionalization of tertiary phosphine and diphosphine ligands improves the selectivity of some catalytic processes.[3] In view of this, we describe herein a metal-assisted synthesis of new diphosphinoketenimines of the type [(PPh$_2$)$_2$C═C═NR] (**5a**, R = Ph; **5b**, R = ^{t}Bu), derived from one of the simplest and most readily available diphosphines, dppm (bis(diphenylphosphino)methane). We also report herein some preliminary results on the reactivity of these ligands.

As shown in Scheme 1, dppm coordinated to manganese(I) in the cationic complex **1** is deprotonated by KOH, in CH$_2$Cl$_2$ as solvent, to give the diphosphinomethanide derivative **2**,[4] which further reacts with I$_2$ and KOH to afford **3**, a neutral complex containing the anionic ligand [(PPh$_2$)$_2$CI]$^-$.[5,6] In a sense, which is useful for the understanding of the present reaction pathway, this ligand can be described as being formed by a diphosphinocarbene fragment [(PPh$_2$)$_2$C:] and the anion I$^-$ (see below). **3** is quantitatively converted to the ketenimine derivative **4**,[5,7] either by standing in CH$_2$Cl$_2$ at room temperature (R = Ph) or by refluxing in toluene (R = ^{t}Bu). A possible mechanism for this interesting transformation is included in Scheme 1. First, we propose that **3** undergoes a change in the coordination mode of the ligand [(PPh$_2$)$_2$CI]$^-$ from η^2-(P,P′) to η^2(P,C) to give intermediate **I**; this type of bonding for diphosphinomethanides is well-documented

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[1] (a) Puddephatt, R. J. *Chem. Soc. Rev.* **1983**, *12*, 99. (b) Chaudret, B.; Delavaux, B.; Poilblanc, R. *Coord. Chem. Rev.* **1988**, *86*, 191. (c) Cotton, F. A.; Hong, B. *Prog. Inorg. Chem.* **1992**, *40*, 179.

[2] Pignolet, L. H. *Homogeneous Catalysis with Metal Phosphine Complexes*; Plenum Press: New York, 1983.

[3] (a) See ref 2, p 239, and references therein. (b) Hayashi, T.; Kanehira, K.; Tsuchiya, H.; Kumada, M. *J. Chem. Soc., Chem. Commun.* **1982**, 1162. (c) Hayashi, T.; Kanehira, K.; Hagihara, T.; Kumada, M. *J. Org. Chem.* **1988**, *53*, 113. (d) Sawamura, M.; Nagata, H.; Sakamoto, H., Ito, Y. *J. Am. Chem. Soc.* **1992**, *114*, 2586.

[4] The synthesis of complexes of type **1** and **2** has been described in: Ruiz, J.; Riera, V.; Vivanco, M.; García-Granda, S.; García-Fernández, A. *Organometallics* **1992**, *11*, 4077.

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in the literature.[8] The second step involves dissociation of iodide, affording the $\eta^2(P,C)$-diphosphinocarbene intermediate **II**.[9] Finally, the coupling of this carbene with coordinated isocyanide would form the new diphosphinoketenimine, with I^- completing the octahedral coordination around manganese to yield **4**. The coupling of carbenes and isocyanides, either free or coordinated to a metal center, is a well-established method of generating ketenimines,[10] and this knowledge offers support for the above proposal, although neither **I** nor **II** have been detected in the reaction mixture. Owing to the presence of CO and CNR groups in these complexes, major information is gained by monitoring the reactions by IR spectroscopy;[5,7] of note is the disappearance of the ν(CN) band of the coordinated isocyanide at 2172 (**3a**) and 2148 cm^{-1} (**3b**) on going from **3** to **4**. The structure of **4b** was definitively established by an X-ray diffraction study.[11] The structure is shown in Figure 1, together with the most important bond distances and angles. The Mn atom is in an octahedral arrangement with the diphosphi-

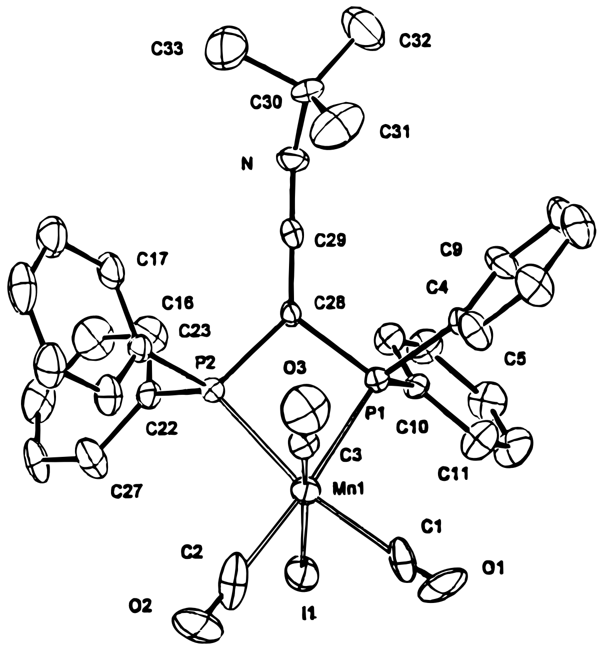

Figure 1. ORTEP view of the molecular structure of the complex $[MnI(CO)_3[(PPh_2)_2C{=}C{=}N^tBu]$ (**4b**), together with the atomic numbering scheme. The ellipsoids for the atoms are drawn at the 30% probability level. The I1 atom and the trans carbonyl C3−O3 are partially interchanged. Important bond distances (Å) and angles (deg): Mn1−I1 = 2.617(2), Mn1−P1 = 2.338(3), Mn1−P2 = 2.339(3), P1−C28 = 1.811(10), P2−C28 = 1.819(9), C28−C29 = 1.305(15), N−C29 = 1.194(14), N−C30 = 1.489(15); P1−Mn−P2 = 72.6(1), P1−C28−P2 = 99.3(4), C28−C29−N = 175.0(12), C29−N−C30 = 131.3(10).

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(5) Typical synthetic procedures are as follows. **3b**: a solution of **2b** (0.30 g, 0.49 mmol) in 20 mL of CH_2Cl_2 was added dropwise to a stirred solution of iodine (0.19 g, 0.74 mmol) in 5 mL of CH_2Cl_2. The resulting mixture was vigorously stirred with an excess of KOH (1 g, 18 mmol) for 1 h. The solution was then filtered off, and the solvent was evaporated to dryness, affording a yellow solid. Yield: 0.33 g, 90%. Anal. Calcd for $C_{33}H_{29}IMnNO_3P_2$: C, 54.19; H, 4.00; N, 1.91. Found: C, 53.95; H, 3.99; N, 1.94. **4b**: a suspension of **3b** (0.40 g, 0.54 mmol) in 25 mL of toluene was refluxed for 10 min. After this time, an orange solution was formed which was concentrated under vacuum to about 7 mL and cooled to −15 °C to obtain orange needles of **4b**. Yield: 0.36 g, 90%. Anal. Calcd for $C_{33}H_{29}IMnNO_3P_2$: C, 54.19; H, 4.00; N, 1.91. Found: C, 54.03; H, 3.86; N, 1.72. Suitable crystals for X-ray analysis were obtained from a dichloromethane solution layered with hexane. **5b**: a solution of 0.3 g of **4b** (0.41 mmol) in 25 mL of toluene was irradiated with visible−UV light at 10 °C for 3 h. The solvent was then removed under vacuum and the remaining solid chromatographed through an alumina column (activity III) prepared in hexane. Elution with toluene/hexane (1/2) gave a colorless fraction, which was evaporated to dryness, giving a white solid. This was recrystallized from hexane at −20 °C. Yield: 63 mg, 33%. Mp: 118 °C. Anal. Calcd for $C_{30}H_{29}NP_2$: C, 77.40; H, 6.38; N, 3.01. Found: C, 77.27; H, 6.20; N, 3.02. **6**: to a solution of **4a** (0.30 g, 0.40 mmol) in 20 mL of CH_2Cl_2 was added phenyl isocyanide (50 mg, 0.48 mmol). After the mixture was stirred at room temperature for 12 h, the color of the solution changed from orange to dark red. The solvent was evaporated to dryness and the residue washed with hexane (3 × 10 mL) to provide a dark red solid. Yield: 0.31 g, 90%. Anal. Calcd for $C_{42}H_{30}IMnN_2O_3P_2$: C, 59.04; H, 3.54; N, 3.28. Found: C, 58.83; H, 3.62; N, 3.15. Suitable crystals for X-ray analysis were obtained from a saturated solution of **6** in a mixture of THF/toluene/hexane. Detailed synthetic procedures for all compounds and additional characterization data are provided in the Supporting Information.

(6) The synthesis of the closely related complex $[Mn(CO)_4\{(PPh_2)_2CI\}]$ has been reported elsewhere: Ruiz, J.; Araúz, R.; Riera, V.; Vivanco, M.; García-Granda, S.; Menéndez-Velázquez, A. *Organometallics* **1994**, *13*, 4162.

(7) Key spectroscopic and analytical data are as follows. **4a**: FTIR (CH_2Cl_2) ν(CO) 2015 (vs), 1954 (s), 1920 (s) cm^{-1}; ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 52.6 (t, $^1J_{C-P}$ = 26 Hz, *C*=C=NPh), 154.8 (t, $^2J_{C-P}$ = 8 Hz, C=*C*=NPh); $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2) δ 22.2 (s). Anal. Calcd for $C_{35}H_{25}NIO_3P_2Mn$: C, 55.95; H, 3.35; N, 1.86. Found: C, 56.23; H, 3.46; N, 2.01. **4b**: FTIR (CH_2Cl_2) ν(CO) 2016 (vs), 1950 (s), 1917 (s) cm^{-1}; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 1.32 (s, $C(CH_3)_3$); ^{13}C NMR (CD_2Cl_2) δ 47.6 (t, $^1J_{C-P}$ = 29 Hz, *C*=C=N^{t}Bu), 144.6 (t, $^2J_{C-P}$ = 7 Hz, C=*C*=N^{t}Bu); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 18.5 (s). Anal. Calcd for $C_{33}H_{29}NIO_3P_2Mn$: C, 54.19; H, 4.00; N, 1.91. Found: C, 54.59; H, 4.19; N, 1.82. **5a**: FTIR (Nujol) ν(CCN) 1997 cm^{-1} (m); ^{13}C NMR (toluene/D_2O) δ 50.4 (t, $^1J_{C-P}$ = 39 Hz, *C*=C=NPh), 174.72 (t, $^2J_{C-P}$ = 7 Hz, C=*C*=NPh); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ −9.8 (s). **5b**: FTIR (Nujol) ν(CCN) 2002 cm^{-1} (s); ^{1}H NMR (CD_2Cl_2) δ 0.74 (s, $C(CH_3)_3$); ^{13}C NMR (CD_2Cl_2) δ 47.5 (t, $^1J_{C-P}$ = 34 Hz, *C*=C=N^{t}Bu), 167.5 (t, $^2J_{C-P}$ = 5 Hz, C=*C*=N^{t}Bu), 30.1 (s, C(*C*H$_3$)$_3$), 58.8 (s, *C*(CH$_3$)$_3$); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ −10.5 (s). Anal. Calcd for $C_{30}H_{29}NP_2$: C, 77.40; H, 6, 38; N, 3.01. Found: C, 77.29; H, 6.20; N, 3.20. **6**: FTIR (CH_2Cl_2) ν(CO) 2013 (vs), 1948 (s), 1916 (s) cm^{-1}; ^{13}C NMR (CD_2Cl_2) δ 98.4 (dd, $^1J_{C-P}$ = 28 Hz, $^1J_{C-P}$ = 23 Hz, P$_2$*C*=C), 146.2 (dd, $^2J_{C-P}$ = 6 Hz, $^2J_{C-P}$ = 4 Hz, P$_2$C=*C*), 156.1 (dd, $^3J_{C-P}$ = 7 Hz, $^3J_{C-P}$ = 4 Hz, *C*=NPh); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 29.9 (d, $^2J_{P-P}$ = 10 Hz), 18.4 (d, $^2J_{P-P}$ = 10 Hz). Anal. Calcd for $C_{42}H_{30}N_2IO_3P_2Mn$: C, 59.04; H, 3.54; N, 3.28. Found: C, 59.28; H, 3.37; N, 3.15.

(8) Karsch, H. H.; Grauvogl, G.; Deubelly, B.; Müller, G. *Organometallics* **1992**, *11*, 4238 and references therein.

(9) A similar coordination mode for a diphosphinocarbene has been found in the complex $[Cp_2Zr\{C(PMe_2)_2\}]_2$: Karsch, H. H.; Grauvogl, G.; Kawecki, M.; Bissinger, P. *Organometallics* **1993**, *12*, 2757.

(10) (a) Aumann, R. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1456. (b) Moloy, K. G.; Fagan, P. J.; Manriquez, J. M.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 56. (c) Igau, A.; Baceiredo, A.; Trinquier, G.; Bertrand, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 621.

(11) Crystal data for $C_{33}H_{29}IMnNO_3P_2$ (**4b**) at 22 °C: monoclinic, space group $P2_1/n$, $a = 11.629(3)$ Å, $b = 20.177(5)$ Å, $c = 14.134(4)$ Å, $\beta = 94.68(2)°$, $Z = 4$, $\rho_{calcd} = 1.470$ g cm^{-3}, μ(Mo Kα) = 14.62 cm^{-1}; diffractometer, Philips PW 1100; radiation, graphite-monochromated Mo Kα ($\lambda = 0.710\ 73$ Å). A total of 7186 reflections were collected in the range $3 < \theta < 27°$ ($\pm h,k,l$). Of these, 2265 having $I > 2\sigma(I)$ were used in the structure solution. $R = 0.0567$, $R_w = 0.0664$, $w = 0.661/[\sigma^2(F_o) + 0.0018F_o^2]$. The I1 atom and the trans carbonyl C3−O3 have been found to be partially interchanged (refined occupancy factor 0.68). All non-hydrogen atoms, except those of the disordered carbonyl C3−O3, were refined anisotropically. All hydrogen atoms were placed at their calculated positions and refined “riding” on the corresponding parent atoms. Crystal data for $C_{42}H_{30}IMnN_2O_3P_2 \cdot 2.5C_4H_8O$ (**6**) at 22 °C: monoclinic, space group $P2_1/c$, $a = 12.540(3)$ Å, $b = 21.717(5)$ Å, $c = 37.098(7)$ Å, $\beta = 95.81(2)°$, $Z = 8$, $\rho_{calcd} = 1.368$ g cm^{-3}, μ(Mo Kα) = 9.88 cm^{-1}; diffractometer, Philips PW 1100; radiation, graphite-monochromated Mo Kα ($\lambda = 0.710\ 73$ Å). A total of 29 394 reflections were collected in the range $3 < \theta < 30°$ ($\pm h,k,l$). Of these, 8317 having $I > 2\sigma(I)$ were used in the structure solution. $R = 0.0766$, $R_w = 0.0832$, unit weights in all stages of refinement. Two crystallographically independent, even if very similar, complexes (A and B) are present. Moreover, five THF molecules of solvation have been found. The I1 atom and the trans carbonyl C3−O3 have been found partially interchanged (refined occupancy factor 0.83 for complex A and 0.64 for complex B). All non-hydrogen atoms, except C3B, O3B, C3B′, O3B′, C13B−C18B, and C13C−C18C (this phenyl was found disordered and distributed in two positions of equal occupancy factor) and the atoms of the THF molecules, were refined anisotropically. All hydrogen atoms (except those of the disordered phenyl group and of the THF molecules) were placed at their calculated positions and refined “riding” on the corresponding parent atoms.

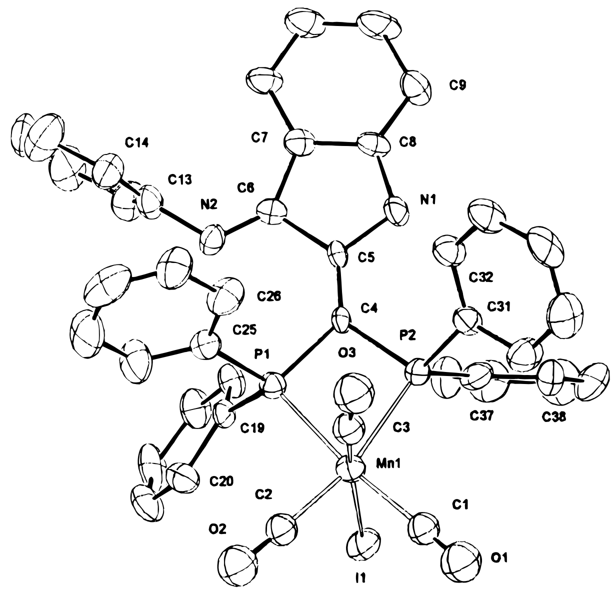

Figure 2. ORTEP view of the molecular structure of one of the two crystallographically independent complexes $[MnI(CO)_3[(PPh_2)_2C{=}\overline{C{-}C({=}NPh)(o\text{-}C_6H_4)N}H]$ (**6A**), together with the atomic numbering scheme. The ellipsoids for the atoms are drawn at the 30% probability level. The I1 atom and the trans carbonyl C3−O3 are partially interchanged. Important bond distances (Å) and angles (deg): Mn1−I1 = 2.687(2) [2.752(3)], Mn−P1 = 2.329(4) [2.328(4)], Mn−P2 = 2.329(3) [2.321(3)], P1−C4 = 1.810(9) [1.805(10)], P2−C4 = 1.805(10), [1.822(11)], C4−C5 = 1.361(14) [1.355(15)], N1−C5 = 1.401(12) [1.430(14)]; P1−Mn−P2 = 72.1(1) [72.4(1)], P1−C4−P2 = 98.6(4) [98.4(5)]. The values in brackets refer to complex **6B**.

noketenimine ligand chelating through the P atoms. The bond lengths and angles along the C28−C29−N−C30 skeleton are similar to those found in most free ketenimines,[12] indicating that there is not a substantial change in these structural parameters on coordination.

The ligands $[(PPh_2)_2C{=}C{=}NR]$ (**5a**,**b**) could be removed from the metal by irradiation of toluene solutions of **4a,b** with visible−UV light. Upon workup, the free diphosphines were isolated as a pale yellow oil (**5a**) and a white microcrystalline solid (**5b**) in 30−40% yield.[5,7] Ketenimines and other heterocumulenes are among the most reactive organic functionalities,[13] and this feature makes the diphosphinoketenimines **5a,b** promising substrates for the synthesis of new functionalized diphosphines. A preliminary result which anticipates the rich chemistry of these ligands is provided by the reaction of **4a** with phenyl isocyanide resulting in a [4 + 1] cycloaddition, followed by migration of the ortho hydrogen to nitrogen to give **6**,[5] a neutral complex containing a unique 2-(diphosphinomethylidene)-3-imino-2,3-dihydroindole ligand (see Scheme 1).[14] The analytical and spectroscopic data for **6** were in accordance with this formulation,[7] but in order to fully structurally characterize the new ligand, an X-ray diffraction study of complex **6** was carried out.[11] A view of the structure is shown in Figure 2, together with the most important bond distances and angles.

It must be noted that so far we have not been able to isolate the above diphosphinoindole as a free ligand, because, on trying to remove this from the metal, degradation of the molecule invariably occurs, giving a complex mixture of species from which only the known tetraphosphine $[(PPh_2)_2C{=}C(PPh_2)_2]$[15] and free phenyl isocyanide appear to be spectroscopically recognized. This result is not very surprising, because the diphosphinoindole in **6** is formally assembled by coupling of 2 equiv of CNPh with the carbene $[(PPh_2)_2C{:}]$.

It is expected that the synthetic methodology described herein can be extended to a number of cationic dppm−manganese(I) complexes bearing two-electron ligands other than isocyanide in that axial position (CO, PR_3, NCR, etc.). This may allow the metal-assisted synthesis of a variety of diphosphines functionalized at the central carbon atom (ketenes, ylides, azirines, etc.). Furthermore, we must emphasized the importance of the ligands $[(PPh_2)_2C{=}C{=}NR]$ themselves, not only because they are rare examples of ketenimines but also because they are highly reactive molecules which show promise in for the preparation of other functionalized diphosphines.

Acknowledgment. We thank the Spanish DGICYT (Project PB91-0678) for financial support.

Supporting Information Available: Text giving detailed experimental procedures and spectroscopic and analytical data for **3**−**6** and tables of atomic coordinates and thermal parameters, all bond distances and angles, and experimental data for the X-ray diffraction studies (Tables SI−IX) for complexes **4b** and **6** (17 pages). Ordering information is given on any current masthead page.

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(13) Tennant, G. In *Comprehensive Organic Chemistry*; Sutherland, I. O., Ed.; Pergamon Press: Oxford, U.K., 1979; Vol. 2, pp 513−590.

(14) For other [4 + 1] cycloaddition reactions of *N*-arylketenimines and isocyanides, see for instance ref 9a.

(15) Anderson, D. M.; Hitchcock, P. B.; Lappert, M. F. *J. Organomet. Chem.* **1989**, *363*, C7.