ORGANOMETALLICS

Insertion of zerovalent metals in the carbon-nitrogen bonds of N,N'-bridged porphyrins

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Organometallics, **1983**, 2 (12), 1888-1889• DOI: 10.1021/om50006a036 • Publication Date (Web): 01 May 2002

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N.W., Washington, DC 20036

4a (R_3 = $CH(CH_3)CO_2$-*t*-Bu), 87533-77-5; **4b**, 87533-78-6; **4c**, 87533-80-0; **4d**, 87533-79-7; **9** (R_1 = H, R_2 = OMe, R_3 = $C(CH_3)_2CN$), 87533-83-3; **9e**, 87533-82-2; **9f**, 87533-81-1; **14**, 87555-32-6; **15**, 87533-85-5; $LiC(CH_3)_2CN$, 50654-53-0; $LiC(CH_3)_2CO_2Et$, 42492-52-4; $LiC(CH_3)_2CO_2Li$, 16423-62-4; $LiCH(CH_3)CO_2$-*t*-Bu, 35717-09-0; 2-(3-oxo-cyclopent-1-yl)-2-phenyl-1,3-dithiane, 66124-79-6; α,α-dimethyl-5-formylcyclohex-2-ene-acetonitrile, 87533-84-4; (η^4-1,3-cyclohexadiene)tricarbonyliron, 12152-72-6; 2-phenyl-2-lithio-1,3-dithiane, 53178-41-9.

Insertion of Zerovalent Metals into the C–N Bonds of N,N′-Bridged Porphyrins

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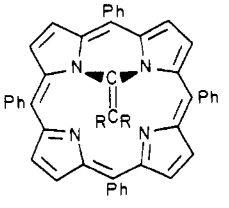
Received May 18, 1983

Summary: Treatment of the N,N′-bridged tetraphenylporphyrin (TPPC=C(*p*-$ClC_6H_4)_2$) with $Fe_3(CO)_{12}$ or $Ru_3(CO)_{12}$ yields the metallocarbene complexes TPPM{C=C(*p*-$C_6H_4Cl)_2$} in which both N–C bonds are broken, while a similar reaction with $Ni(CO)_4$ yields TPP{C=C(*p*-$C_6H_4Cl)_2$}Ni in which only one N–C bond is broken.

Recent work has demonstrated that the pyrrolic nitrogen atoms in metalloporphyrins have considerable reactivity. Examples of this include the reversible transfer of alkyl or aryl groups between the metal and nitrogen in iron or cobalt porphyrins[1] and the reversible insertion of carbene ligand, which initially resided on the iron, into an Fe–N bond.[2] We report here that the C–N bonds of N,N′-bridged porphyrin **1**[3,4] are reactive toward insertion of low-valent metals and that, depending on the metal, one or both of the C–N bonds can be broken. The only previous report of reaction of N,N′-dialkylated porphyrins with metal ions have resulted in the formation of porphyrin complexes that utilize the unalkylated nitrogens as donors and that leave the N,N′ bridge intact.[5] The oxidative addition of C–N bonds to low-valent transition metals is a rare occurrence.



1, R = *p*-ClC_6H_4

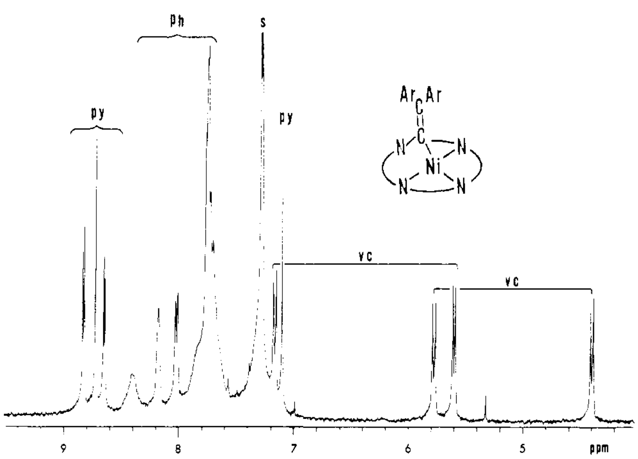
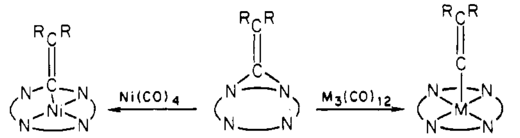


Figure 1. The 360-MHz ^1H NMR spectrum of **4** in chloroform-*d* solution at 21 °C. Peaks are labeled as follows: py, pyrrole protons; Ph, phenyl protons of the tetraphenyl porphyrin; VC, phenyl protons of the *p*-chlorophenyl groups; S, residual, undeuterated solvent resonance.

Scheme I



4 **1** **2**, M = Fe
3, M = Ru

Our results are summarized in Scheme I. Treating the N,N′-bridged porphyrin **1** with an excess of $Fe_3(CO)_{12}$ in boiling tetrahydrofuran solution for 1–2 h followed by concentration, chromatography on silica gel with benzene as eluent, and crystallization from dichloromethane/acetonitrile yields the red carbene complex **2** in 90% yield. The spectroscopic properties of **2** (electronic spectrum, 416 (ϵ 1.29 × 10^5), 520 (1.44 × 10^4), 542 nm (sh); ^1H NMR 8.70 (s, 8 H), 8.12 (s, 4 H), 7.7 (m, 16 H), 6.43 (d, *J* = 7.9 Hz, 4 H), 4.01 ppm (d, *J* = 7.9 Hz, 4 H)) are in good agreement with previous observations of this material obtained by a path reported earlier.[6,7] The reaction between **1** and an equimolar quantity of $Ru_3(CO)_{12}$ under similar conditions yields the red carbene complex **3** that elutes as the first chromatographic band, in 40% yield.[8] The spectroscopic properties of this new substance (electronic spectrum, 416 (ϵ 7.19 × 10^4), 522 (1.52 × 10^4) 542 nm (sh); ^1H NMR spectrum 8.67 (s, 8 H), 8.09 (s, 4 H), 7.69 (s, 8 H), 7.67 (s, 8 H), 6.42 (d, *J* = 8.0 Hz, 4 H), 3.99 ppm (d, *J* = 8.0 Hz, 4 H)) are similar to those of its iron analogue **2**.

The reaction of **1** with $Ni(CO)_4$ takes a different course, in which only one of the C–N bonds is broken. Treatment of **1** with excess $Ni(CO)_4$ in boiling tetrahydrofuran yields, under similar workup, dark green crystals of **4** in 90% yield.[9] The molecular composition of **4** is established from its field-desorption mass spectrum which exhibits a multiplet at *m/e* 916 (for $^{58}Ni^{35}Cl_2$) due to the parent ion and weak features at *m/e* 670 due to nickel(II) tetraphenylporphyrin, and at *m/e* 246 due to $(p\text{-}ClC_6H_4)_2C_2$. The ^1H NMR spectrum is shown in Figure 1. The two *p*-chlorophenyl groups of the vinyl bridge appear as two quartets that have chemical shifts upfield of normal phenyl resonances because of ring current shifts from the por-

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(6) Mansuy, D.; Lange, M.; Chottard, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 3213.

(7) This reaction completes the cycle TPPFe{C=C$(C_6H_4Cl)_2$} → {TPPC=C$(C_6H_4Cl)_2$}FeCl → 1 → TPPFe{C=C$(C_6H_4Cl)_2$}.

(8) Anal. Calcd for $C_{58}H_{36}Cl_2N_4Ru$: C, 72.50; H, 3.78; N, 5.83; Cl, 7.38. Found: C, 72.73; H, 4.09; N, 6.72; Cl, 7.20.

(9) Anal. Calcd for $C_{58}H_{36}Cl_2N_4Ni$: C, 75.84; H, 3.95; N, 6.10; Cl, 7.72. Found: C, 75.65; H, 4.18; N, 5.92; Cl, 7.78.

phyrin. In accord with its symmetry, there are four pyrrole chemical shifts resulting from the four distinct pyrrole hydrogens. Spin–spin splitting (^1J(H,H) = 4.9 Hz) due to the presence of two distinct types of protons on two of the pyrrole rings results in the appearance of an AB pattern at 8.7 and 8.85 ppm. At 25 °C some of the phenyl resonances of the tetraphenylporphyrin are broadened (those at 8.4, 8.2, and 7.8 ppm) due to averaging resulting from rotation of the phenyl groups. These lines narrow, reversibly, on cooling to −30 °C. The electronic spectrum of 4 in benzene solution consists of absorptions at 426 (ϵ 9.36 × 10^4) and 554 nm (7.47 × 10^3). These properties are consistent with those of a related species (prepared by an entirely different route), with a carbene moiety inserted into the N–Ni bond of a nickel porphyrin.[10] Moreover, the formation of 4 for d^8 nickel and the contrasting preparation of 2 and 3 for d^6 iron and ruthenium are entirely in accord with theoretical predictions on the relative stabilities of these two structural types for different electron counts.[11]

Preliminary results indicate that other low-valent metal compounds also react with 1, and a study of the scope of insertions into these highly reactive C–N bonds is in progress.

Acknowledgment. We thank the National Institute of Health (Grant GM-26266) for support and Professor A. L. Burlingame, Director, Mass Spectrometry Resource UCSF, for the field description mass spectra.

Registry No. 1, 87532-88-5; 2, 72042-21-8; 3, 87532-89-6; 4, 87532-90-9; $Fe_3(CO)_{12}$, 17685-52-8; $Ru_3(CO)_{12}$, 15243-33-1; $Ni(CO)_4$, 13463-39-3.

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Heterobimetallic Iridium or Rhodium μ-Bis(diphenylphosphino)methane Complexes with Copper(I), Silver(I), or Gold(I). A Silver Hydride Complex and the Crystal Structure of $[(PhC\equiv C)(OC)Ir(\mu\text{-}Ph_2PCH_2PPh_2)_2CuCl]$

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Received August 9, 1983

Summary: $[Ir(dppm)_2CO]Cl$ (dppm = $Ph_2PCH_2PPh_2$) is used to produce a variety of mixed Ir–Cu, –Ag, –Au, or –Rh complexes containing μ-dppm while $[Rh(dppm)_2CO]Cl$ gives a mixed rhodium–silver complex; the d^{10} metal ions are readily displaced by Ir(I) or Rh(I) (d^8) in transmetalation reactions, and a molecular hydride of silver has been obtained.

We have described systematic syntheses of heterobimetallic complexes of platinum(II)[1,2] or palladium(II),[3] bridged to other metals by $Ph_2PCH_2PPh_2$ (dppm). In the present communication we describe syntheses of heterobimetallic complexes of iridium(I) or rhodium(I) bridged to other metals by dppm which are surprisingly specific and fast considering that the starting complexes $[M(dppm)_2CO]Cl$ (M = Ir or Rh) are coordinatively saturated.[4] Treatment of the readily prepared[5] $[Ir(dppm)_2(CO)]Cl$ with $CuC\equiv CPh$ in boiling acetone for 30 min gives $[(PhC\equiv C)(OC)Ir(\mu\text{-}dppm)_2CuCl]$ (**1a**) as red prisms in 68–72% yield.[6] The $^{31}P\{^1H\}$ NMR spectrum (CH_2Cl_2) is broad at +20 °C, but at −60 °C it shows the expected AA′BB′ splitting pattern: $\delta(P_A)$ +21.5, $\delta(P_B)$ −22.0 ($N = |^2J(P_AP_B) + {}^4J(P_AP_{B'})| = 98$ Hz). We associate the broadening at +21 °C with rapid phosphine exchange at

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[1] McEwan, D. M.; Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1982**, 1240 and references therein. Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1983**, 889. Langrick, C. R.; McEwan, D. M.; Pringle, P. G.; Shaw, B. L. *Ibid.* **1983**, in press.

[2] Cooper, G. R.; Hutton, A. T.; McEwan, D. M.; Pringle, P. G.; Shaw, B. L. *Inorg. Chim. Acta* **1983**, *76*, L265. Blagg, A.; Hutton, A. T.; Pringle, P. G.; Shaw, B. L. *Ibid.* **1983**, *76*, L267.

[3] Langrick, C. R.; Pringle, P. G.; Shaw, B. L. *Inorg. Chim. Acta* **1983**, *76*, L263.

[4] Spectral data and elemental analyses for the complexes described herein.

1a: IR (KBr, cm^{-1}) $\nu(C\equiv O)$ 1985 (s), $\nu(C\equiv C)$ 2100 (vw); $^1H\{^{31}P\}$ NMR ($CDCl_3$, −50 °C) δ 4.39 (d, *J* = 12.7 Hz, PC*H*P), 3.54 (d, *J* = 12.7 Hz, PC*H*P); $^{31}P\{^1H\}$ NMR ($CDCl_3$, −60 °C) $\delta(P_A)$ +21.5, $\delta(P_B)$ −22.0 (*N* = 98 Hz). Anal. Calcd for $C_{59}H_{49}ClCuIrOP_4$: C, 58.8; H, 4.1. Found: C, 58.8; H, 4.5.

1b: IR (KBr, cm^{-1}) $\nu(C\equiv O)$ 1985 (s), $\nu(C\equiv C)$ 2090 (vw); $^1H\{^{31}P\}$ NMR ($CDCl_3$, +21 °C) δ 4.3 (br s, PC*H*P), 3.7 (br s, PC*H*P); $^{31}P\{^1H\}$ NMR ($CDCl_3$, −30 °C) $\delta(P_A)$ +19.9, $\delta(P_B)$ (CD_2Cl_2, ($^1J(^{109}AgP_B)$ = 430 Hz, $^1J(^{107}AgP_B)$ = 374 Hz, *N* = 95 Hz). Anal. Calcd for $C_{59}H_{49}AgClIrOP_4\cdot{}^1/_8CH_2Cl_2$: C, 57.1, H, 4.0; Cl, 3.6. Found: C, 57.0; H, 3.95; Cl, 3.4.

1c: IR (KBr, cm^{-1}) $\nu(C\equiv O)$ 1985 (s), $\nu(C\equiv C)$ not observed; $^1H\{^{31}P\}$ NMR ($CDCl_3$, −50 °C) δ 4.52 (d, *J* = 12.7 Hz PC*H*P), 3.58 (d,d, *J* = 12.7 Hz, ^3J(AgH) = 6.9 Hz, PC*HP*), 2.30 (s, C*H*$_3$); $^{31}P\{^1H\}$ NMR ($CDCl_3$, −30 °C) $\delta(P_A)$ +20.0, $\delta(P_B)$ −12.9 ($^1J(^{109}AgP_B)$ = 430 Hz, $^1J(^{107}AgP_B)$ = 371 Hz, *N* = 95 Hz). Anal. Calcd for $C_{59}H_{49}AgClIrOP_4\cdot{}^1/_4CH_2Cl_2$: C, 57.1; H, 4.1; Cl, 2.85. Found: C, 57.75; H, 4.0; Cl, 2.6.

1d: $^{31}P\{^1H\}$ NMR ($CDCl_3$, −50 °C) $\delta(P_A)$ +24.2, $\delta(P_B)$ −11.3 ($^1J(^{109}AgP_B)$ = 437 Hz, $^1J(^{107}AgP_B)$ = 378 Hz, *N* = 93 Hz).

2a: IR (KBr, cm^{-1}) $\nu(C\equiv O)$ 1975, $\nu(C\equiv C)$ not observed; $^1H\{^{31}P\}$ NMR ($CDCl_3$, +21 °C) δ 4.54 (d, *J* = 14.0 Hz, PC*H*P), 4.44 (d, *J* = 14.0 Hz, PC*H*P); $^{31}P\{^1H\}$ NMR ($CDCl_3$, +21 °C) $\delta(P_A)$ +14.6, $\delta(P_B)$ +32.3 (*N* = 59 Hz).

2b: IR (KBr, cm^{-1}) $\nu(C\equiv O)$ 1968, 1985 (s), $\nu(C\equiv C)$ 2090 (vw); $^1H\{^{31}P\}$ NMR ($CDCl_3$, +21 °C) δ 4.05 (br s, PC*H*P), 3.89 (br s, PC*H*P); $^{31}P\{^1H\}$ NMR ($CDCl_3$, +21 °C) $\delta(P_A)$ +18.6, $\delta(P_B)$ +2.0 ($^1J(^{109}AgP_B)$ = 542 Hz, $^1J(^{107}AgP_B)$ = 469 Hz, *N* = 73 Hz). Anal. Calcd for $C_{83}H_{69}AgBIrOP_4\cdot{}^1/_2CH_2Cl_2$: C, 64.3; 64.3; H, 4.6; Cl, 2.3. Found: C, 64.0; H, 4.85; Cl, 2.2.

3: $^{31}P\{^1H\}$ NMR ($CDCl_3$, +21 °C) $\delta(P_A)$ −1.6, $\delta(P_B)$ +16.3 ($^1J(AgP_B)$ ≈ 200 Hz, *N* = 56 Hz); $^1H\{^{31}P\}$ NMR ($CDCl_3$, +21 °C) +3.96 (d, *J* = 13.5 Hz, PC*H*P), +3.43 (d,d,d, *J* = 13.5, 5.0, 1.2 Hz, PC*H*P) −9.6 (br d, *J*(AgH) = 17 Hz, Ir(μ-*H*)Ag), −11.85 (d, *J* = ~2 Hz, Ir*H*).

4: IR (KBr, cm^{-1}) $\nu(C\equiv O)$ 1964 (vs); $^1H\{^{31}P\}$ NMR ($CDCl_3$, 0 °C) 4.48 (d, *J* = 13.7 Hz, PC*H*P), 4.23 (d, *J* = 13.7 Hz, PC*H*P); $^{31}P\{^1H\}$ NMR ($CDCl_3$, +21 °C) $\delta(P_A)$ +18.6, $\delta(P_B)$ +31.0 (*N* = 56 Hz). Anal. calcd for $C_{51}H_{44}AuCl_2IrOP_4$: C, 48.75; H, 3.5; Cl, 5.6. Found: C, 48.4; H, 3.5; Cl, 6.3.

5a: IR (KBr, cm^{-1}) $\nu(C\equiv O)$ 1968 (vs); $^1H\{^{31}P\}$ NMR ($CDCl_3$, +21 °C) 4.26 (d, *J* = 13.2 Hz, PC*H*P), 3.38 (d, *J* = 13.2 Hz, PC*H*P); $^{31}P\{^1H\}$ NMR ($CDCl_3$, +21 °C) $\delta(P_A)$ +24.3, $\delta(P_B)$ −11.3 ($^1J(^{109}AgP_B)$ = 439 Hz, $^1J(^{107}AgP_B)$ = 381 Hz, *N* = 93 Hz). Anal. Calcd for $C_{51}H_{44}AgCl_2IrOP_4$: C, 52.45; H, 3.80; Cl, 6.1. Found: C, 52.3; H, 3.95; Cl, 6.2.

5b: IR (KBr, cm^{-1}) $\nu(C\equiv O)$ 1970 (vs); $^{31}P\{^1H\}$ NMR ($CDCl_3$, −50 °C) $\delta(P_A)$ +26.3, $\delta(P_B)$ −21.5 (*N* = 95 Hz). Anal. Calcd for $C_{51}H_{44}Cl_2CuIrOP_4$: C, 54.5; H, 4.2; Cl, 6.3. Found: C, 54.3; H, 4.2; Cl, 6.7.

5c: IR (KBr, cm^{-1}) $\nu(C\equiv O)$ 1982, 1995 (sh); $^1H\{^{31}P\}$ NMR ($CDCl_3$, 0 °C) 4.33 (d, *J* = 12.7 Hz, PC*H*P), 3.81 (d,d, *J* = 12.7 Hz, ^3J(AgH) or ^3J(RhH) = 5.8 Hz, PC*H*P); $^{31}P\{^1H\}$ NMR ($CDCl_3$, −50 °C) $\delta(P_A)$ +29.9 ($^1J(RhP_A)$ = 122 Hz), $\delta(P_B)$ −7.7 ($^1J(^{109}AgP_B)$ = 449 Hz, $^1J(^{107}AgP_B)$ = 391 Hz, *N* = 103 Hz). Anal. Calcd for $C_{51}H_{44}AgCl_2OP_4Rh$: C, 56.75; H, 4.1; Cl, 6.5. Found: C, 56.45; H, 4.2; Cl, 6.6.

6a: IR (KBr, cm^{-1}) $\nu(C\equiv O)$ 2065, 1993 (vs), 1850 (w), 1760; $^1H\{^{31}P\}$ NMR ($CDCl_3$, +21 °C) 4.48 (d, *J* = 13.7 Hz, PC*H*P), 3.81 (d, *J* = 13.7 Hz, PC*H*P); $^{31}P\{^1H\}$ NMR ($CDCl_3$, −50 °C) $\delta(P_A)$ +28.3 ($^1J(RhP_A)$ = 97 ($^1J(RhP_A)$ $\delta(P_B)$ +1.1 (*N* = 88 Hz). Anal. Calcd for $C_{53}H_{44}Cl_2IrO_3P_4Rh\cdot{}^1/_2CH_2Cl_2$: C, 50.9; H, 3.6; Cl, 8.45. Found: C, 50.45; H, 3.6; Cl, 8.15. It is likely that **6a** is contaminated with **7** since the μ-CO ligand is readily lost.

7: $^{31}P\{^1H\}$ NMR ($CDCl_3$, −50 °C) $\delta(P_A)$ +17.3 ($^1J(RhP_A)$ = 124 Hz), $\delta(P_B)$ −6.7 (*N* = 105 Hz).

[5] Miller, J. S.; Caulton, K. G. *Inorg. Chem.* **1975**, *14*, 1067.

[6] In a typical experiment, a mixture of $[Ir(dppm)_2(CO)]Cl$ (0.20 g, 0.195 mmol) and the d^{10} metal complex (e.g., $CuC\equiv CPh$, $[AgCl(PPh_3)]_4$) (1 equiv) in acetone (5 cm^3) was boiled under reflux for 20–30 min. The precipitated product was filtered off, washed with cold acetone, and dried in vacuo. The products so obtained gave good elemental analyses and were shown to be pure by their NMR spectra (see ref 4).

0276-7333/83/2302-1889$01.50/0