to the appropriate initial pressure with a 1:1 CO–H_2 mixture. The reaction was heated externally in an oil bath at 70 °C and then stopped after 24 h. The vessal was vented and opened to the air. NMR experiments were performed directly on the reaction solution.

Acknowledgment. Financial support of the Biomedical Research Support Grant RR07062, Division of Research Resources, National Institutes of Health, administered by the Research Challenge Fund of New York University, and a loan of rhodium salts from Platina Laboratories are gratefully acknowledged.

Supplementary Material Available: Tables of NMR data and nomenclature and elemental analytical results for all new compounds (3 pages). Ordering information is given on any current masthead page.

Contribution from the Max-Planck-Institut für Kohlenforschung, D-4330 Mülheim a. d. Ruhr, West Germany

(1,4-Diazabutadiene)nickel(0) Complex $(2,6\text{-}iPr_2C_6H_3N{=}CHCH{=}NC_6H_3\text{-}2,6\text{-}iPr_2)Ni(CO)_2$

Klaus R. Pörschke,* Werner Bonrath, and Richard Mynott

Received May 22, 1990

Recently, the synthesis and the electronic absorption and resonance Raman spectra, as well as the MO diagram[1] and the low-temperature photochemistry,[2] of the (1,4-diazabutadiene)nickel(0) carbonyl complex $(2,6\text{-}iPr_2Ph\text{-}dad)Ni(CO)_2$ (**1**) [$2,6\text{-}iPr_2Ph\text{-}dad$ = 1,4-bis(2,6-diisopropylphenyl)-1,4-diazabutadiene] have been reported in this journal. The authors stated that the compound was obtained by reaction of $Ni(cod)_2$ (cod = 1,5-cyclooctadiene) with an equimolar amount of $2,6\text{-}iPr_2Ph\text{-}dad$ [to yield intermediate $(2,6\text{-}iPr_2Ph\text{-}dad)Ni(cod)$[3]] and prolonged exposure to CO with final purification by column chromatography. Only small amounts of **1** were obtained by this route, and synthesis attempts were often not successful.[4] On the basis of the resonance Raman spectra, a "pseudoplanar" coordination geometry of the nickel center has been suggested for **1**.[1] These reports[1,2] have prompted us to communicate our findings on the synthesis, reactivity, and characterization of **1**.

Our interest in complex **1** arose from the fact that the highly reactive $(2,6\text{-}iPr_2Ph\text{-}dad)Ni$–alkene complexes $(2,6\text{-}iPr_2Ph\text{-}dad)Ni(C_2H_4)_2$ and $(2,6\text{-}iPr_2Ph\text{-}dad)Ni(\eta^2,\eta^2\text{-}1,5\text{-}hexadiene)$[5] react rapidly at low temperature (−70 °C) with *4* equiv of CO (1 bar) to yield $Ni(CO)_4$, displaced $2,6\text{-}iPr_2Ph\text{-}dad$, and alkene. We found that even $Ni(2,6\text{-}iPr_2Ph\text{-}dad)_2$ reacts with CO (20 °C, 1 bar, 2 days) under displacement of *both* $2,6\text{-}iPr_2Ph\text{-}dad$ ligands to yield $Ni(CO)_4$.[6] It did not appear possible to stop the reactions at the stage of the presumably transient complex **1**. However it could be shown that **1** is easily obtained by the *reverse* reaction. By the method of Bock and tom Dieck,[7] $Ni(CO)_4$ (11 mmol) and $2,6\text{-}iPr_2Ph\text{-}dad$ (10 mmol) react in pentane (60 mL) under gentle reflux slowly (7 h) with evolution of CO to afford an intense violet reaction solution (reflux condenser cooled to −30 °C to trap $Ni(CO)_4$), from which upon cooling to 0 °C violet crystals of **1** separate in 70% yield.[8] An excess of $2,6\text{-}iPr_2Ph\text{-}dad$ should be avoided when the reaction is carried out, since it cocrystallizes with **1**.

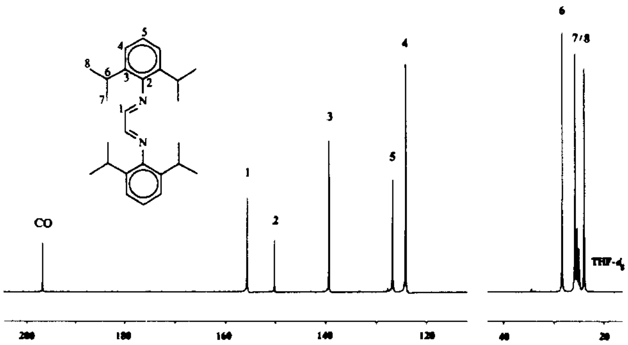
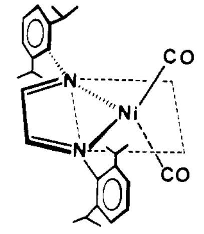


Figure 1. 75.5-MHz $^{13}C\{^1H\}$ NMR spectrum of $(2,6\text{-}iPr_2Ph\text{-}dad)Ni(CO)_2$ (**1**) in THF-d_8 at −30 °C.



1

As can already be expected from the above, **1** itself reacts rapidly and quantitatively at 20 °C with 2 equiv of CO to yield $Ni(CO)_4$.[9] The reaction resembles a titration, since at the end of the reaction the color suddenly changes from violet to orange-yellow. Obviously, even a small amount of **1** produces an intensively colored solution. Equation 1 represents an equilibrium

$$Ni(CO)_4 + 2,6\text{-}iPr_2Ph\text{-}dad \rightleftharpoons \underset{\mathbf{1}}{(2,6\text{-}iPr_2Ph\text{-}dad)Ni(CO)_2} + 2CO \quad (1)$$

that lies at 1 bar of CO pressure far to the left side. This explains the difficulties the authors of refs 1 and 2 experienced with the reaction procedure applied by them.

Complex **1**[10] is stable at room temperature (mp 150 °C) and only moderately sensitive to air. In the MS spectrum (70 eV, 85 °C) the largest observable masses correspond to $M^+ - CO$ (462, 15%) and $M^+ - 2CO$ (434, 100%; for ^{58}Ni). The IR, UV/vis, and ^1H NMR (CD_2Cl_2, −60 °C) data reported[1] for **1** have been confirmed, but well-resolved ^1H NMR spectra may also be obtained at 27 °C (THF-d_8). The 75.5-MHz ^{13}C NMR spectrum (THF-d_8, −30 °C) of **1** (Figure 1) contains eight sharp signals for the $2,6\text{-}iPr_2Ph\text{-}dad$ ligand.[11] There is no significant change in the spectra on reducing the temperature to −110 °C, so that it is improbable that the spectrum is a time average of different conformations in rapid equilibrium. The spectra are in accordance with a C_{2v} symmetry of the complex, the plane of the phenyl rings being perpendicular to the Ni,N,N coordination plane. Within each iPr substituent the two methyl groups are inequivalent be-

---

(1) Servaas, P. C.; Stufkens, D. J.; Oskam, A. *Inorg. Chem.* **1989**, *28*, 1774.

(2) Servaas, P. C.; Stufkens, D. J.; Oskam, A. *Inorg. Chem.* **1989**, *28*, 1780.

(3) tom Dieck, H.; Svoboda, M.; Greiser, T. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1981**, *36*, 823. Svoboda, M. Dissertation, Universität Frankfurt/Main, 1978.

(4) Stufkens, D. J. Private communication.

(5) Bonrath, W.; Pörschke, K. R.; Michaelis, S. *Angew. Chem.* **1990**, *102*, 295; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 298.

(6) Bonrath, W.; Pörschke, K. R.; Mynott, R.; Krüger, C. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1990**, *45*.

(7) Bock, H.; tom Dieck, H. *Angew. Chem.* **1966**, *78*, 549; *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 520.

(8) According to the IR data file of this institute, compound **1** has been obtained previously by K. Radine but was not examined closer (1984).

(9) Displacement of a 1,4-diazabutadiene ligand from nickel by CO has recently also been described: Sinnema, J. C. M.; Fendesak, G. H. B.; tom Dieck, H. *J. Organomet. Chem.* **1990**, *390*, 237.

(10) Anal. Calcd for $C_{28}H_{36}N_2NiO_2$ (M_r = 491.3): C, 68.45; H, 7.39; N, 5.70; Ni, 11.95; O, 6.51. Found: C, 68.51: H, 7.23; N, 5.66; Ni, 11.91. IR: (KBr) several absorptions in the C≡O stretching region probably due to packing effects; (*n*-hexane) $\nu(CO)$ 2022 (A_1), 1970 cm^{-1} (B_1). UV/vis (benzene): λ_{max} = 333 (ϵ = 3740), 543 nm (6320 L mol^{-1} cm^{-1}). ^1H NMR (200 MHz, THF-d_8, 27 °C): δ 8.21 (s, 2 H, CH=N), 7.27 (s, 6 H, phenyl), 3.00 (septet, 4 H, $CHMe_2$), 1.30, 1.15 (both d, 12 H, CH_3). ^{13}C NMR (75.5 MHz, THF-d_8, −30 °C): δ 196.7 (2 C, CO), 155.6 (2 C, CH=N), 150.1 (2 C, Ph_{ipso}), 139.3 (4 C, Ph *o*-C), 126.7 (2 C, Ph *p*-C), 124.1 (4 C, Ph *m*-C), 28.3 (4 C, $CHMe_2$), 25.7, 23.8 (both 4 C, CH_3).

(11) Essentially the same spectrum is observed at 50.3 MHz and 27 °C for both THF-d_8 and benzene-d_6.

0020-1669/90/1329-5008$02.50/0 © 1990 American Chemical Society

cause of the hindered rotation of the phenyl groups about the C–N axes. Therefore, if an improbable strictly square-planar coordination is not considered, the ^{13}C NMR spectrum is consistent with a C_{2v} tetrahedral structure of complex 1 in solution but not with a static "pseudoplanar" structure (C_2), for which 13 carbon signals would be expected for the 2,6-iPr$_2$Ph-dad ligand.

Contribution from the Laboratoire de Chimie
Organo-Minérale, UA 422 au CNRS,
Institut de Chimie, F-67008 Strasbourg, France

Synthesis of Functionalized Asymmetrical Bis(terpyridine)osmium(II) Complexes under Mild Conditions

Jean-Paul Collin,* Stêphane Guillerez, and Jean-Pierre Sauvage*

Received April 13, 1990

Introduction

The synthesis of (terpy)$_2$ complexes of osmium(II) (terpy = 2,2′:6′,2″-terpyridine) containing two differently substituted ligands at their 4′-position can be carried out in two successive steps,[1] using classical reactions.

$$\mathrm{OsCl_3 + terpy\text{-}X \xrightarrow[\text{ethanol, }\Delta]{} Os(terpy\text{-}X)Cl_3} \qquad (1)$$

$$\mathrm{Os(terpy\text{-}X)Cl_3 + terpy\text{-}Y \xrightarrow[\text{ethylene glycol}]{\text{refluxing}} Os(terpy\text{-}X)(terpy\text{-}Y)^{2+}} \qquad (2)$$

X, Y = substituents on the 4′-position of the terpy ligands

Due to the extreme stability of the Os(III)–Cl bond, the conditions of reaction 2 have to be particularly vigorous[2,3] whereas reaction 1 leads to monoterpy complexes under mild conditions.[4] In general, the preparation of OsN_6^{2+} complexes (N_6 represents six aromatic imine functions) requires long reaction times and high temperatures.[5] This method is unadapted to ligands bearing little robust chemical groups, as those used for building diades (diade = donor–acceptor linked system) and triades aimed to photoinduced charge separation[1,6] (Chart I). In the present paper, we report a new and very mild method allowing preparation of asymmetrical bis(2,2′:6′,2″-terpyridine)osmium(II) complexes in a stepwise procedure.

Experimental Section

All products were of reagent grade and were used as received. Acetonitrile (SDS) and tetrahydrofuran (SDS) were used without purification. The ligands Me-phterpy, Br-phterpy, and MeO-phterpy (phterpy = 4′-phenyl-2,2′:6′,2″-terpyridine) were prepared by modification of literature procedures[7] and purified by the method of Constable et al.[8] The ligands PTZ-phterpy (PTZ = phenothiazine–CH$_2$–) and PQ^{2+}-phterpy (PQ^{2+} = *N*-methyl-*N*′-methylene-4,4′-bipyridinium, paraquat) were synthesized as described previously.[1] The ligand Diaa-phterpy (Diaa = di-*p*-anisylamino) was obtained in the same way as Me-phterpy[7] by condensation of 2 equiv of 2-acetylpyridine with 1 equiv of *p*-(bis(*p*-methoxyphenyl)amino)benzaldehyde.

Chart I

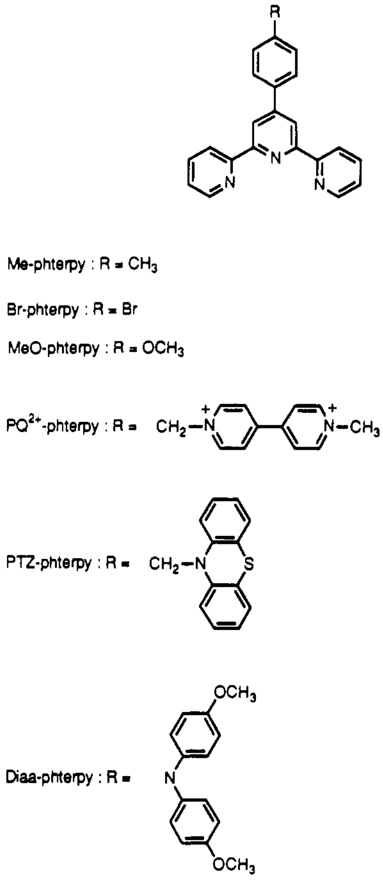


Table I

complex	yield, % *a*	yield, % *b*
Os(Me-phterpy)$_2^{2+}$		31
Os(Me-phterpy)(MeO-phterpy)$^{2+}$	66	49
Os(Me-phterpy)(Br-phterpy)$^{2+}$	35	32
Os(Me-phterpy)(PQ^{2+}-phterpy)$^{4+}$		48
Os(Me-phterpy)(PTZ-phterpy)$^{2+}$	17	8.5
Os(Me-phterpy)(Diaa-phterpy)$^{2+}$	35	17

[a] Reducing agent: Pt(0)/H$_2$. [b] Reducing agent: hydrazine.

The latter compound was synthesized by formylation of bis(*p*-methoxyphenyl)phenyl amine[9] according to Walter et al.[10] ^1H NMR spectra were acquired on a Bruker WP200SY instrument. Chemical shifts are reported vs. Me$_4$Si as an internal standard. Visible and UV spectra were obtained on a Kontron spectrophotometer. Cyclic voltammetry was carried out on a Bruker E1310 potentiostat connected to a XY Ifelec IF3802 recorder. FAB spectra were obtained by using a VG instruments ZAB-HF mass spectrometer. Elemental analyses of C, H, and N were performed by the Service de l'Institut de Chimie de Strasbourg.

Synthesis of the Complexes. Preparation of Os(Me-phterpy)(O)$_2$(OH)(NO$_3$)·H$_2$O. To an aqueous solution of Me-phterpy (88 mg in 120 mL) at pH = 3 (HNO$_3$) was added, in 5 h, 1 equiv of K$_2$Os(O)$_2$(OH)$_4$ in solid form. The pH of the solution was maintained at 3 ± 0.2 by HNO$_3$ during the addition. The solution was stirred overnight. After filtration on Millipore, the filtrate was reduced to 60 mL, and 10 mL of an aqueous saturated solution of KNO$_3$ was added. The pale green precipitate was filtered, washed with 10 mL of cold water, and dried under vacuum. Yield: 92%.

^1H NMR (CD$_3$OD): δ 9.62 (dd, 2 H), 9.01 (s, 2 H), 8.86 (d, 2 H), 8.67 (t, 2 H), 8.27 (t, 2 H), 8.80 (d, 2 H), 8.26 (d, 2 H), 2.41 (s, 3 H).

FAB MS (nitrobenzyl alcohol matrix): m/z = 564 [Os(Me-phterpy)(O)$_2$(OH)$^+$].

Anal. Calcd for Os(Me-phterpy)(O)$_2$(OH)(NO$_3$)H$_2$O: C, 40.00; H, 3.35; N, 8.48. Found: C, 40.08; H, 3.79; N, 8.62.

---

(1) Collin, J. P.; Guillerez, S.; Sauvage, J. P. *J. Chem. Soc., Chem. Commun.* **1989**, 776.
(2) Morgan, G.; Burstall, F. H. *J. Chem. Soc.* **1937**, 1649.
(3) Kober, E. M.; Sullivan, B. P.; Dressick, W. J.; Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 7383.
(4) Buckingham, D. A.; Dwyer, F. P.; Sargeson, A. M. *Aust. J. Chem.* **1961**, *14*, 250.
(5) Klassen, D. M.; Hudson, C. W.; Shaddix, E. L. *Inorg. Chem.* **1975**, *14*, 2733.
(6) Danielson, E.; Eliott, C. M.; Merkert, J. W.; Meyer, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 2519.
(7) Case, F. H.; Butte, W. A. *J. Chem. Soc.* **1961**, 4415. Spahni, W.; Calzaferri, G. *Helv. Chim. Acta* **1984**, *67*, 450.
(8) Constable, E. C.; Ward, M. D.; Corr, S. *Inorg. Chim. Acta* **1988**, *141*, 201.
(9) Wieland, H. *Ber. Dtsch Chem. Ges.* **1910**, *43*, 705.
(10) Baker, T. N.; Doherty, W. P.; Kelley, W. S.; Newmeyer, W.; Rogers, J. E.; Spalding, R. E.; Walter, R. I. *J. Org. Chem.* **1965**, *30*, 3714.

0020-1669/90/1329-5009$02.50/0