Supplementary Material Available: Tables SI-SV, listing crystallographic data, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen coordinates and isotropic thermal parameters for **3** (8 pages); Table SVI, listing observed and calculated structure factors for **3** (38 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
New York University, New York, New York 10003

Practical Syntheses of Chelating Bis(dioxaphospholane) Ligands through Chlorodioxaphospholane Intermediates and Demonstration of Catalytic Competence of Bis(phosphite)rhodium Cations

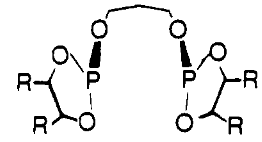
Donald J. Wink,* Thomas J. Kwok, and Allen Yee

Received February 1, 1990

The development of novel mono- and diphosphorus compounds, either for their inherent physical properties[1] or for application to catalysis[2] (in particular, asymmetric catalysis[3]) continues as an important area of synthetic phosphorus research. Most of the compounds that have been developed for catalytic applications are derivatives of aryl- or alkylphosphines; suprisingly little work has been done with less electron-rich ligands, such as phosphites or related species. These are a very tempting group of compounds for catalysis, since oxygenated phosphorus ligands may cause dramatic changes in the reactivity or selectivity of a catalyst by making the metal more electrophilic. In addition, appropriately functionalized chiral alcohols, particularly chiral diols, constitute a synthetically diverse means of quickly, (in some cases) without the need for a discrete resolution, synthesizing new chiral auxiliaries.[4] Finally, the absence of a P–C bond in a ligand may permit the synthesis of catalysts that are not degraded by oxidative P–C bond cleavage, a significant problem in hydroformylation.[5]

These advantages are balanced somewhat by certain important problems. A less electron-rich metal center may not undergo the oxidative-addition reactions that are the key to small molecule activation. Also, while the P–O bond may be more stable to simple oxidative-insertion reactions, it is still quite susceptible to hydrolysis, alcoholysis, or Arbuzov-type side reactions. In this paper, we report how we have successfully addressed this synthetic challenge in the moderate-scale synthesis of one group of compounds, bis(dioxaphospholane) ligands (**1**) derived from a chiral diol side group and an achiral backbone.[6] Moreover, cationic rhodium complexes of these ligands are indeed competent for the generation of both hydrogenation and hydroformylation catalysts.

R = CO_2Et, CO_2Pr^i, Ph



1

Results and Discussion

Simple chiral diols—we have worked with diisopropyl tartrate, diethyl tartrate, and (*R*,*R*)-dihydrobenzoin[7]—react readily with PCl_3 in the presence of base to give a chlorodioxaphospholanes[8] as a single stereoisomer (eq 1). In the case of the tartrate esters,

$$\mathrm{PCl_3 + HOCHRCHROH + 2py \xrightarrow{Et_2O\ or\ THF} 2py{\cdot}HCl + Cl\overline{P(OCHRCHRO})} \quad (1)$$

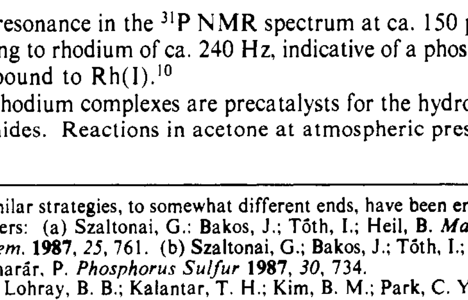
the product is purified by distillation in vacuo while the diphenyl derivative is obtained pure after crystallization from ether. All three compounds are obtained in analytically pure form in fair to good (46–93%) yield. They are sensitive to protic solvents but are indefinitely stable at ambient temperatures under dry nitrogen.

The formation of a bis(dioxaphospholane) could conceivably be performed with any other diol. However, reactions with aliphatic 1,2-diols such as ethylene glycol and pinacol are complicated by the decomposition reactions, presumably involving an equilibrium mixture of heterocyclic rings. Much better results are obtained with 1,3-propanediol, which affords good (71–90%) yields of the desired diphosphorus products as oils (eq 2) that can be

$$\mathrm{Cl\overline{P(OCHRCHRO}) + HOCH_2CH_2CH_2OH + 2py \xrightarrow{Et_2O\ or\ THF} 2PyHCl + \mathbf{1}} \quad (2)$$

purified to spectroscopic and analytical purity from ether. The NMR spectra of these complexes are essentially the same as their acyclic analogues (shifts in the ^{31}P NMR spectrum occur at ca. 145 ppm). They are thermally sensitive, but can be stored at low temperature and handled for short periods at ambient temperatures.

Our primary interest in these compounds is as auxiliaries for asymmetric catalysis, and indeed they easily form cationic rhodium precatalysts. Reaction with bis(1,5-cyclooctadiene)rhodium tetrafluoroborate gives good yields of analytically and spectroscopically pure complex salts (eq 3).[9] These exhibit a characteristic resonance in the ^{31}P NMR spectrum at ca. 150 ppm with a coupling to rhodium of ca. 240 Hz, indicative of a phosphite-like ligand bound to Rh(I).[10]



(3)

The rhodium complexes are precatalysts for the hydrogenation of enamides. Reactions in acetone at atmospheric pressure and

---

(1) (a) Pastor, S. D.; Togni, A. *Inorg. Chim. Acta* **1989**, *159*, 3. (b) Pastor, S. D.; Hyun, J. L.; Odorisio, P. A.; Rodebaugh, R. K. *J. Am. Chem. Soc.* **1988**, *110*, 6547.

(2) Pignolet, L. H. *Homogeneous Catalysis with Metal Phosphine Complexes*, Plenum: New York, 1983.

(3) These include the following methods. Hydrogenation: (a) Knowles, W. S. *Acc. Chem. Res.* **1983**, *16*, 106. (b) Halpern, J. *Science* **1982**, *217*, 401. (c) Ohta, T.; Takaya, H.; Noyori, R. *Inorg. Chem.* **1988**, *27*, 566. Palladium-catalyzed allylation: (d) Auburn, P. R.; Mackenzie, P. B.; Bosnich, B. *J. Am. Chem. Soc.* **1985**, *107*, 2033. (e) Mackenzie, P. B.; Whelan, J.; Bosnich, B. *J. Am. Chem. Soc.* **1985**, *107*, 2046. (f) Trost, B. M.; Murphy, D. J. *Organometallics* **1985**, *4*, 1143. (g) Hayashi, T.; Yamamoto, A.; Hagihara, T.; Ito, Y. *Tetrahedron Lett.* **1986**, *27*, 191. Hydroformylation: (h) Parrinello, G.; Stille, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 7122. (i) Hobbs, C. F.; Knowles, W. S. *J. Org. Chem.* **1981**, *44*, 22. Decarboxylation: (j) Consiglio, G.; Scalone, M.; Rama, F. *J. Mol. Catal.* **1989**, *50*, L11. Aldol condensations: (k) Pastor, S. D.; Togni, A. *J. Am. Chem. Soc.* **1989**, *111*, 2333.

(4) (a) Brunner, H. *J. Organomet. Chem.* **1986**, *300*, 39. (b) Kagan, H. B. In *Asymmetric Synthesis*; Morrison, J. S., Ed., Academic: New York, 1985; Vol. 5, p 1.

(5) Dubois, R. A.; Garrou, P. E. *Organometallics* **1986**, *5*, 466.

(6) Similar strategies, to somewhat different ends, have been employed by others: (a) Szaltonai, G.; Bakos, J.; Tőth, I.; Heil, B. *Magn. Reson. Chem.* **1987**, *25*, 761. (b) Szaltonai, G.; Bakos, J.; Tőth, I.; Pelczer, I.; Soharár, P. *Phosphorus Sulfur* **1987**, *30*, 734.

(7) (a) Lohray, B. B.; Kalantar, T. H.; Kim, B. M.; Park, C. Y.; Shibata, T.; Wai, J. S. M.; Sharpless, K. B. *Tetrahedron Lett.* **1989**, *30*, 2041. (b) Jacobsen, E. N. Markő, I.; Mungall, W. S.; Schröder, G.; Sharpless, K. B. *J. Am. Chem. Soc.* **1988**, *110*, 1968.

(8) (a) Lucas, H. J.; Mitchell, F. W.; Scully, C. N. *J. Am. Chem. Soc.* **1950**, *72*, 5491. (b) Edmundson, R. S. *Chem. Ind.* (*London*) **1965**, 1220. Other terms that have been for these compounds are used are phosphochloridites, dioxaphospholes, and cyclic phosphites.

(9) The phosphorus ligand, once coordinated to rhodium, seems quite stable thermally.

(10) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 2397.

0020-1669/90/1329-5006$02.50/0

ambient temperature at a substrate:catalyst ratio of 200:1 proceed in a few hours to give good (>90%) yields of the hydrogenated product. The enantiospecificity of the hydrogenation is, however, quite poor, with ee's on the order of 2–10%. This is not unexpected because the chiral induction probably requires a more crowded metal ligand environment *at the metal* and a smaller chelate ring[11] than that afforded by the dioxaphospholane group.

The reactions of these complexes and hydrogen, in the presence or absence of enamide substrate, are quite different from those of related bis(diphenylphosphino) ligands. If the complexes themselves are treated directly with hydrogen, a black deposit formed. The same thing happens at the *conclusion* of the catalytic hydrogenation reactions (control experiments show that the actual hydrogenation reaction is probably homogeneous: the reaction is not poisoned by Hg(0)[12] and the black deposit is *not* kinetically component as a catalyst for olefin hydrogenation). It is not dissolved by any cleaning agent except chromic acid in sulfuric acid. Combustion analysis indicates that this material contains a substantial amount of carbon and hydrogen (23% and 5%). We speculate that is a polymer of the decomposed ligand and Rh(0).

Monitoring an active hydrogenation reaction in $(CD_3)_2CO$ indicates, surprisingly, that the enamide is hydrogenated *before* the cyclooctadiene[13] and that the black deposit is formed at the time when, *after* the enamide is exhausted, cyclooctane is formed. We have seen new resonances in the ^{31}P NMR at ca. δ 155 assigned as a transient enamide complex.[14]

The complex derived from dihydrobenzoin has also been tested as a precursor in the hydroformylation of olefins. At 70 °C under 350 psi of 1:1 $CO:H_2$ styrene is hydroformylated at a rate of ca. 10 turnovers h^{-1} to give a 3:1 mixture of the iso:*n* aldehyde (examination of the iso aldehyde by chiral shift reagent indicates that it is racemic). This preference for the branched product is not surprising, for the bis(dioxaphospholane) ligand is expected to be relatively uncrowded *at the metal*, and therefore, there is less driving force for the linear, less hindered intermediate. Indeed, we speculate that the more electrophilic metal center is important in the unusual preference for the branched product because the intermediate branched alkyl ligand will be a superior donor to the metal. At the conclusion of the reaction, the solution is a red color, perhaps indicative of a stable Rh(III) species. This is supported by the observation in the spectrum of the actual reaction mixture (at atmospheric pressure) of a single resonance in the ^{31}P NMR spectrum at δ 121 with a J_{Rh-P} = 205 Hz. A shift to higher field and a reduction in the Rh–P coupling has been observed on oxidation of related bis(diphenylphosphino) complexes.[15]

Conclusion

The development of a practical synthesis of bis(dioxaphospholane) ligands and the demonstration that they are competent auxiliaries for catalysis opens up a neglected vein in the rich chemistry of phosphorus ligands. The novel chemoselectivity and promising regioselectivity that have been observed are both attributable to the less electron-rich bis(dioxaphospholane) architecture. They suggest several possible applications, though of course at this stage the ligands will not be useful in asymmetric catalysis. Finally, the ease of synthesis of this architecture makes it an attractive scaffold to design other chiral architectures.[3,4,16] This is especially true given the great versatility available in the synthesis of chiral diols[17] that can now, by using the methods reported here, be readily incorporated into C_2 chiral ligands that with varied and, perhaps, rationally designed structures for other forms of asymmetric catalysis.[18]

Experimental Section

General Data. All procedures, unless otherwise noted, were performed under an atmosphere of prepurified nitrogen by using standard glovebox and Schlenk techniques. Solvents were stored under nitrogen after drying and distillation. Diethyl ether and THF were dried over sodium benzophenone ketyl; chloroform was dried twice with Na_2SO_4; pentane and methylene chloride were dried with CaH_2. Acetone was distilled from anhydrous K_2CO_3 and stored over activated 3-Å molecular sieves.

Phosphorus trichloride (Mallinkrodt), the tartrate esters (Chemical Dynamics), and the eneamide substrates (Aldrich) were used as purchased. Propane-1,3-diol and styrene were distilled under reduced pressure and stored under nitrogen. (*R,R*)-Dihydrobenzoin was synthesized, purified, and confirmed to be optically pure by using the published procedures of Sharpless and co-workers.[7] Pyridine (Aldrich, anhydrous grade) was used as obtained. NMR data, elemental analysis results (Schwartzkopf Microanalytical Labs Woodside, NY), and nomenclature are given in the supplementary material.

Synthetic Procedures. In each case, a detailed experimental procedure is provided for the dihydrobenzoin derivative, with any notes concerning the tartrate esters following.

Synthesis of 2-Chloro-1,3,2-dioxaphospholanes. Phosphorus trichloride (3.2 g, 23 mmol) was dissolved in 60 mL of THF. A solution of (*R*,*R*)-dihydrobenzoin (5.00g, 23.4 mmol) and anhydrous pyridine (4 ml, 51 mmol) in 60 mL of THF was added dropwise while the reaction flask was cooled in an ice–water bath. The resulting white suspension was stirred overnight at room temperature and then filtered. The product was isolated as spectroscopically pure colorless crystals (5.1 g, 80%) after crystallization from diethyl ether at −78 °C.

The tartrate ester derivatives were synthesized by addition of the PCl_3 solution to the diol/pyridine solution, and superior yields were obtained if the reaction was left to stir for several days. The clear, colorless filtrate was concentrated in vacuo and the crude product purified by vacuum (ca. 10^{-3} Torr) distillation. Typical yields of purified products: from diethyl tartrate; 93% (bp 93–95 °C (10^{-3} Torr); from diisopropyl tartrate, 46% (bp 108–110 °C).

Synthesis of Propane-Bridged Bis(dioxaphospholane)s. The chlorodioxaphospholane (3.00 g, 11 mmol) was dissolved in 20 mL of THF. This solution was immersed in ice–water, and with stirring, a solution of 1,3-propanediol (0.41 g, 5.4 mmol) and anhydrous pyridine (1 ml, 0.013 mol) in 15 mL of THF was added dropwise over a period of 30 min. The mixture, which turns into a white suspension, was stirred for an addition 3 h and then filtered. The solvent was removed in vacuo and the product purified by extraction with ether, filtration, and concentration to give a colorless, spectroscopically pure oil (2.8 g, 90%). Typical yields of purified products: from diethyl tartrate, 77%; from diisopropyl tartrate, 71%.

Synthesis of (1,5-Cyclooctadiene)(bis(dioxaphospholane))rhodium(I) Tetrafluoroborates. The bis(dioxaphospholane) (0.69 g, 1.2 mmol) was dissolved in 5 mL of methylene chloride and added, via cannula, to a solution of bis(1,5-cyclooctadiene)rhodium(I) tetrafluoroborate (0.50 g, 1.23 mmol) in 10 mL of CH_2Cl_2. The bright orange solution was concentrated in vacuo, and the residue was extracted with chloroform. Product was precipitated from solution by the addition of Et_2O (0.88 g, 83%). Typical yields of purified products: from diethyl tartrate, 54%; from diisopropyl tartrate, 55%.

Catalysis Reactions. For hydrogenation, the reactions were conducted in either a 100- or 250-mL round-bottomed flask fitted with two stopcock valves. The prochiral olefin and (bis(dioxaphospholane))rhodium complex were weighed into the flask and dissolved in acetone (stored over molecular sieves after distillation from K_2CO_3) in the glove box. The flask was evacuated and refilled with hydrogen; the reaction was magnetically stirred. For the methyl acrylate substrate, monitoring by TLC was sufficient to show the completion of the reaction, within 1–2 h. Reactions of cinnamic acid and methyl cinnamate substrates took 8–10 h, and their conclusion was indicated by the appearance of a black deposit. It was also shown that this black deposit did not independently catalyze hydrogenation at reasonable rates.

The hydroformylation reactions were performed by loading substrate and catalysts into a bomb in an inert atmosphere and then pressurizing

---

[11] Landis, C. R.; Halpern, J. *J. Organomet. Chem.* **1983**, *250*, 485.

[12] Whitesides, G. M.; Hackett, M.; Brainard, R. L.; Lavalleye, J.-P. P. M.; Sowinski, A. F.; Izumi, A. N.; Moore, S. S.; Brown, D. W.; Staudt, E. M. *Organometallics* **1985**, *4*, 1819.

[13] This, in turn, suggests a subtle selectivity in the oxidation addition of H_2: Collman, J. P. *Acc. Chem. Res.* **1968**, *1*, 136.

[14] This is similar to the upfield shift associated with enamide complexes of dppe and its derivatives: (a) Chan, A. S. C.; Pluth, J. J.; Halpern, J. *Inorg. Chim. Acta* **1979**, *37*, L477. (b) Brown, J. M.; Parker, D. *J. Chem. Soc., Chem. Commun.* **1980**, 342.

[15] Browm, J. M.; Chaloner, P. A.; Kent, A. G.; Murrer, B. A.; Nicholson, P. N.; Parker, D.; SIdebottom, P. J. *J. Organomet. Chem.* **1981**, *216*, 263.

[16] Fryzuk, M.; Bosnich, B. *J. Am. Chem. Soc.* **1978**, *100*, 5491.

[17] (a) Cunningham, A. F., Jr.; Kündig, E. P.; *J. Org. Chem.* **1988**, *53*, 1823. (b) Seebach, D.; Kalinowski, H.-O.; Bastani, B.; Crass, G.; Daum, H.; Dörr, H.; DuPreez, N. P.; Ehrig, V.; Langer, W.; Nüssler, C.; Oei, H.-A.; Schmidt, M. *Helv. Chim. Acta* **1977**, *60*, 301.

[18] (a) Bogdan, P. L.; Irwin, J. J.; Bosnich, B. *Organometallics* **1989**, *8*, 1450. (b) Brown, J. M.; Evans, P. L. *Tetrahedron* **1988**, *44*, 4905.

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 vessel 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**.

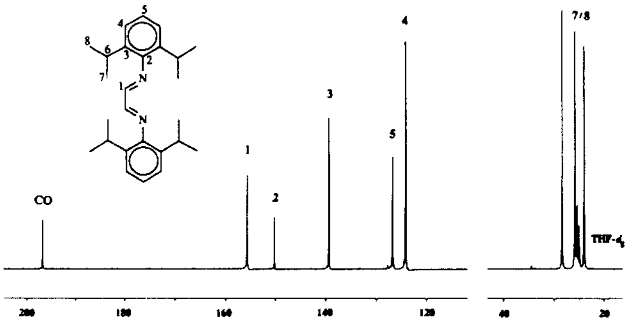
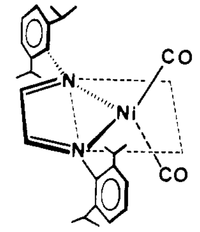


Figure 1. 75.5-MHz $^{13}C\{^1H\}$ NMR spectrum of $(2,6\text{-}iPr_2Ph\text{-}dad)Ni(CO)_2$ (**1**) in THF-d_8 at −30 °C.



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