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A Nickel(0) Dimer/Monomer System with Facile and Reversible Carbon Monoxide Uptake: $Ni_2(CO)_x(dppm)_2$ (x = 3, 4) and $Ni(CO)_3(\eta^1\text{-dppm})$

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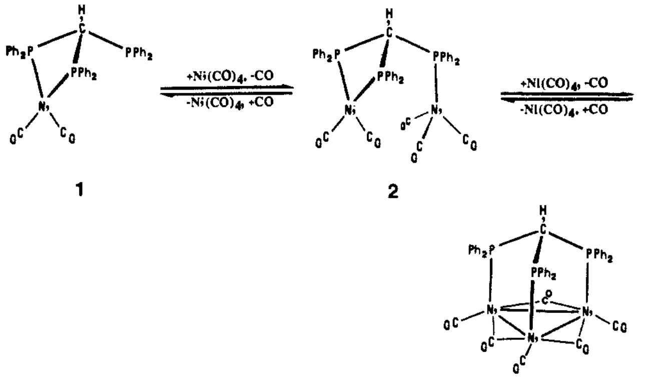
Abstract: $Ni(CO)_2[HC(PPh_2)_3]$ decomposes slowly at room temperature to produce the bis(diphenylphosphino)methane (dppm) bridged nickel(0) dimer $Ni_2(CO)_3(dppm)_2$ (**4**). Complex **4** crystallizes in the orthorhombic space group *Pbcn* with a = 14.015 (2) Å, b = 18.784 (5) Å, c = 22.743 (8) Å, V = 5987 (4) Å^3, and Z = 4. A total of 3913 reflections were collected using Mo Kα radiation, and the structure was solved and refined by using 1237 independent reflections with $F_o^2 > 3\sigma(F_o)^2$, leading to a final R_1 = 0.062. Ignoring the Ni–Ni bond, the structure of **4** shows approximate tetrahedral geometry about the two nickel atoms with an unusual cis arrangement of the two bridging dppm ligands, one bridging carbonyl ligand, and two terminal carbonyl ligands. The molecule sits on a 2-fold axis passing through the bridging carbonyl group, and there are three solvent molecules of benzene per nickel dimer in the unit cell. The Ni–Ni bond distance of 2.603 (4) Å is in the proper range for the expected single bond. **4** readily reacts with 1 equiv of carbon monoxide under ambient conditions to form the 18-electron binuclear complex with terminal CO ligands, $Ni_2(CO)_4(dppm)_2$ (**5**), which has been characterized spectroscopically. Although **5** is a saturated 18-electron species, it also readily reacts with CO to fragment, producing $Ni(CO)_3(\eta^1\text{-dppm})$ (**6**) in which the dppm ligand is only bound by one phosphorus atom. Spectroscopic data on **6** supporting the $Ni(CO)_3(\eta^1\text{-dppm})$ formulation are presented. The CO-based equilibrium **4** $\rightleftharpoons$ **5** $\rightleftharpoons$ **6** is fully reversible in solution.

The coordination chemistry of the tris-phosphine ligand system $HC(PPh_2)_3$ (tripod) has proven to be quite interesting from two fundamental viewpoints. Tripod has the ability to coordinate triangular arrays of transition-metal atoms in clusters and, in doing so, can effect inhibition of cluster fragmentation processes.[1] Tripod can also act as a template for the construction of new clusters as illustrated by the stepwise synthesis of $Ni_3(\mu\text{-CO})_3(CO)_3(\text{tripod})$ (**3**), from $Ni(CO)_4$ and tripod.[2]

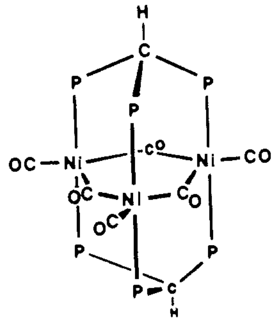


Our further investigations into this Ni system have revealed an unexpected side reaction. Although the coordination of tripod to the triangular face of a cluster usually has a mutually stabilizing effect on both tripod and the cluster complex,[1] tripod can readily fragment under the proper conditions to produce bis(diphenylphosphino)methane (dppm). It has, for example, been reported that the mercury cluster $Hg_3(O_2CCH_3)_6(\text{tripod})$ gradually decomposes in solution to form $[Hg(O_2CCH_3)_2]_2$ and an unidentified white material.[3] The decomposition of tripod to dppm has been confirmed in the case of the related system $[Hg_3(\text{tripod})](O_3SCF_3)_6$ in Me_2SO, which yields $[Hg_2(\mu\text{-dppm})_2](O_3SCF_3)_4$ and $[Hg(\eta^1\text{-dppm})_2](O_3SCF_3)_2$.[3] We report another example of the relatively facile fragmentation of tripod to form dppm, which, in our system, goes on to form the novel dppm-bridged nickel dimer $Ni_2(\mu\text{-CO})(CO)_2(dppm)_2$ (**4**).

Results and Discussion

When a THF solution of $Ni(CO)_4$ and tripod is refluxed, the initially yellow solution of $Ni(CO)_2(\text{tripod})$ rapidly darkens to the orange color of the nickel trimer **3**.[4] If the refluxing is continued, the solution further darkens, eventually turning an intensely deep green or red-black, depending on the exact ratio of $Ni(CO)_4$ to tripod used. A yellow precipitate of **4** gradually forms and can be readily isolated by filtration from the reaction solution.

The presence of a relatively low-frequency bridging carbonyl ligand (ν_{CO} = 1775 cm^{-1}) clearly pointed to an electron-rich dimer or cluster species. Our initial structural assignment was a bis(tripod)-capped nickel trimer with three terminal and bridging CO ligands. The elemental analysis and NMR data were consistent with this formulation, although the carbonyl region in the infrared spectrum did not agree with either D_{3h} (one terminal and one bridging CO band expected) or C_{3v} (two terminal and two bridging bands) symmetry structures. Tripod fragmentation had



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[§] Concordia University.

(1) (a) Arduini, A. A.; Bahsoun, A. A.; Osborn, J. A.; Voelker, C. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 1024. (b) Bahsoun, A. A.; Osborn, J. A.; Voelker, C. *Organometallics* **1982**, *1*, 1114.

(2) Osborn, J. A.; Stanley, G. G. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 1025.

(3) Lusser, M.; Peringer, P. *J. Organomet. Chem.* **1986**, *301*, 269.

(4) This reaction has been followed by infrared spectroscopy and we have observed the initial formation of $Ni(CO)_2(\text{tripod})$, $Ni_2(CO)_5(\text{tripod})$, and $Ni_3(CO)_6(\text{tripod})$ as discussed in ref 2.

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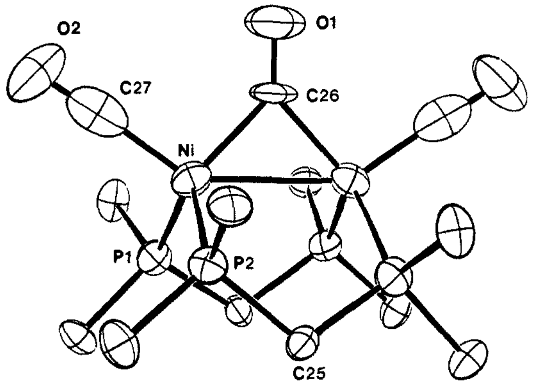

Figure 1. ORTEP plot of $Ni_2(CO)_3(dppm)_2$ (4) with only one carbon atom of each phenyl ring on the dppm ligand shown. Thermal ellipsoids are drawn at the 50% probability level. The molecule is sitting on a twofold rotation axis passing through the bridging carbonyl.

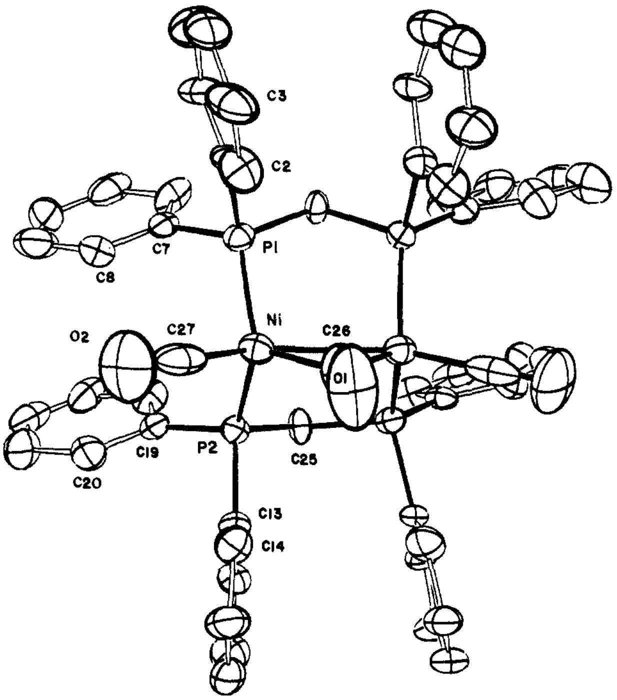

Figure 2. ORTEP plot of the full molecule of **4**.

Table I. Selected Bond Distances (Å) and Angles (Deg) for $Ni_2(\mu\text{-}CO)(CO)_2(dppm)_2$[a]

	Bond Distances		
Ni-Ni′	2.603 (4)	Ni-P1	2.214 (4)
Ni-P2	2.210 (4)	Ni-C26	1.89 (1)
Ni-C27	1.81 (1)	C26-O1	1.10 (2)
C27-O2	1.11 (2)	P1-C1	1.85 (1)
P1-C7	1.79 (1)	P1-C25	1.86 (1)
P2-C25	1.82 (1)	P2-C13	1.82 (1)
P2-C19	1.80 (1)		
	Bond Angles		
Ni1′-Ni1-P1	95.4 (1)	Ni1-C27-O2	176 (1)
Ni1′-Ni1-P2	93.7 (1)	Ni1-P1-C1	114.9 (5)
Ni1′-Ni1-C26	46.4 (4)	Ni1-P1-C7	118.8 (4)
Ni1′-Ni1-C27	145.3 (5)	Ni1-P1-C25	113.7 (4)
P1-Ni1-P2	108.7 (2)	C1-P1-C7	102.0 (6)
P1-Ni1-C26	120.9 (2)	C1-P1-C25	102.2 (6)
P1-Ni1-C27	103.7 (5)	C7-P1-C25	103.2 (6)
P2-Ni1-C26	115.6 (2)	Ni1-P2-C13	115.3 (5)
P2-Ni1-C27	106.7 (5)	Ni1-P2-C19	120.6 (5)
C26-Ni1-C27	99.0 (6)	Ni1-P2-C25	113.8 (5)
P1-C25-P2	107.4 (7)	C13-P2-C19	100.2 (6)
Ni1′-C26-Ni1	87.1 (8)	C13-P2-C25	103.7 (6)
Ni1-C26-O1	136.5 (4)	C19-P2-C25	100.6 (6)
Ni1′-C26-O1	136.5 (4)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. A complete set of bond distances and angles are included in the supplementary material.

not been observed in our previous studies and so, unfortunately, did not receive any serious consideration.

The single-crystal X-ray structure on **4**, however, clearly demonstrates that the cleavage of a PPh_2 group from tripod has indeed occurred to give a dppm-bridged nickel dimer, $Ni_2(\mu\text{-}CO)(CO)_2(dppm)_2$. ORTEP plots of the structure are shown in Figures 1 and 2, while a list of important bond distances and angles is given in Table I. The dimer has a Ni-Ni single bond expected from electron counting with a Ni-Ni distance of 2.603 (4) Å, which is in the upper bond distance range for a Ni-Ni single bond. **4** has two dppm ligands in an unusual cis configuration, as opposed to the now quite common A-frame dimers, which have trans dppm ligands.[5] While a number of cis,trans-dppm dimers have been characterized, e.g., $Rh_2(CO)Cl_2[(PhO)_2PN(Et)P(OPh)_2]_2$,[6] $[Pt_2Me_3(dppm)_2]^+$,[7] $[Ni_2(\mu\text{-}CNCH_3)(CNCH_3)_3]^{2+}$,[8] $Mn_2(CO)_8(dppm)_2$,[9] and $Rh_2(\mu\text{-}CO)(CO)_2(dppm)_2$,[10] the cis,cis-dppm orientation was, until very recently, unknown. Kubiak and coworkers reported the first dimer system with a cis,cis arrangement of dppm ligands, namely, $Ni_2(\mu\text{-}CNCH_3)(CNCH_3)_2(dppm)_2$, and its reactions with electrophiles.[11] Since then several other cis,cis-dppm binuclear complexes have been reported: $Rh_2(\mu,\eta^2\text{-}PhCCPh)(CO)_2(dppm)_2$ by Eisenberg and Berry;[12] $Rh_2Cl_4(dppm)_2$ by Cotton and Dunbar;[13] and $Ir_2(\mu\text{-}CNPh)_2(CNPh)_2(dmpm)_2$ by Kubiak and Wu.[14] Kubiak's $Ni_2(\mu\text{-}CNCH_3)(CNCH_3)_2(dppm)_2$ and our $Ni_2(\mu\text{-}CO)(CO)_2(dppm)_2$ binuclear complexes are both isoelectronic and isostructural and represent a new family of *non*-A-frame systems for $M_2(dppm)_2$ dimers.

The M-M bonded *cis,cis*-$M_2(dppm)_2$ geometry is a very interesting one since it represents the binuclear homogeneous analogue of an edge/corner for a metal surface, while the *trans,trans*-$M_2(dppm)_2$ form is most closely related to the less reactive flat surface.[15] In the cis,cis orientation, the electron-donating phosphine ligands are more or less trans to any incoming ligands, and this should make these dimers more reactive to oxidative addition reactions and for pumping electron density out onto the ligands coordinated to the metal atoms. Kubiak and co-workers have indeed observed such behavior in their $Ni_2(\mu\text{-}CNCH_3)(CNCH_3)_2(dppm)_2$ dimer, which shows remarkable basicity of the bridging isocyanide nitrogen atom with an estimated pK_a of $\simeq 10$ in THF solutions.[11]

Although we have not attempted the synthesis of **4** from dppm and $Ni(CO)_4$, Balch and co-workers have prepared **4** via this route, but the reaction is not straightforward.[16] Kubiak and co-workers prepare the Ni(0) complex $Ni_2(\mu\text{-}CNCH_3)(CNCH_3)_2(dppm)_2$ by sodium amalgam reduction of $[Ni_2(\mu\text{-}CNCH_3)(CNCH_3)_3(dppm)_2]^{2+}$.[11] Most interestingly, the reaction of $Ni_2(\mu\text{-}$

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[5] Cf.: (a) Cowie, M.; Dwight, S. K. *Inorg. Chem.* **1979**, *18*, 2700. (b) Mague, J. L.; Sanger, A. R. *Inorg. Chem.* **1979**, *18*, 2060. (c) Brown, M. P.; Fisher, J. R.; Puddephatt, R. J.; Seddon, K. R. *Inorg. Chem.* **1979**, *18*, 2808. (d) Cowie, M.; Dwight, S. K. *Inorg. Chem.* **1980**, *19*, 2500. (e) Kubiak, C. P.; Eisenberg, R. *Inorg. Chem.* **1980**, *19*, 2726.

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[14] Wu, J.; Kubiak, C. P. Presented at the 192nd National Meeting of the American Chemical Society, Anaheim, CA, Sept 1986; INOR 305.

[15] Muettertles, E. L.; Rhodin, T. N.; Band, E.; Brucker, C. F.; Pretzer, W. R. *Chem. Rev.* **1979**, *79*, 91.

[16] Balch, A. L., private communication.

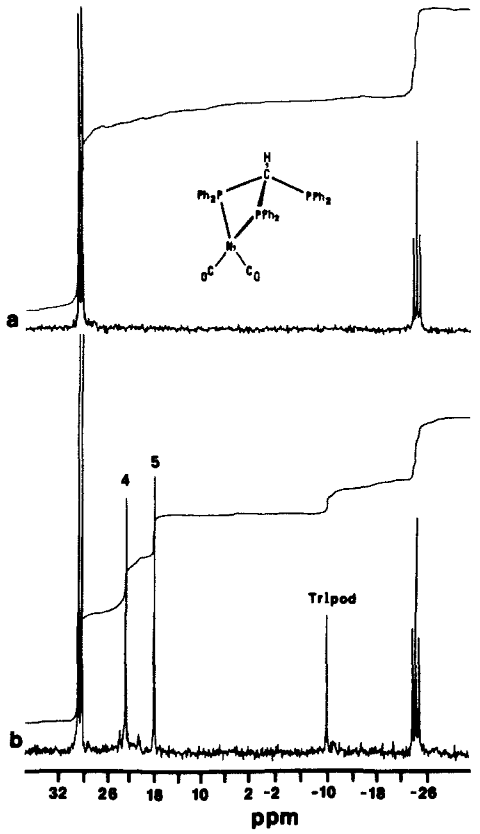


Figure 3. ^{31}P NMR spectra of (a) $Ni(CO)_2$(tripod) and (b) the same solution after 8 days, showing the formation of $Ni_2(CO)_3(dppm)_2$ (4), $Ni_2(CO)_4(dppm)_2$ (5), and free tripod. There is also an unidentified singlet nearly coincident with 5.

$CNCH_3)(CNCH_3)_2(dppm)_2$ with liquid CO_2 at 1500–2200 psi produces 4.[17] Recently, the preparation of 4 has been reported by Holah and co-workers from the reaction of Ni(II) salts, dppm, and $NaBH_3CN$ in the presence of carbon monoxide, thus avoiding the use of $Ni(CO)_4$.[18] The complex Holah isolated, although properly formulated, was proposed to have a traditional trans,trans A-frame geometry.

The production of 4 from the fragmentation of tripod under mild conditions has been demonstrated by taking a benzene/THF solution of the pure monomeric nickel-tripod complex, 1, and allowing it to sit at room temperature for several weeks. The solution gradually turns amber from its original yellow color and deposits well-formed yellow crystals of 4.[19] Two ^{31}P NMR spectra, one of the starting $Ni(CO)_2$(tripod) complex and the other of the same solution after 8 days, are shown in Figure 3. This clearly demonstrates that 4 is indeed being produced from the fragmentation of tripod and *not* from dppm impurities that are sometimes present from the preparation of tripod. We also routinely check the purity of the tripod ligand with ^{31}P NMR, which serves as a sensitive indicator. Although we have not investigated the mechanism, fragmentation most likely involves the homolytic rupture of one of the methine–PPh_2 bonds and hydrogen abstraction by the resulting $Ph_2P(CH^{\bullet})PPh_2$ radical from the THF solvent to produce dppm. Supporting evidence for this comes from the work of Peringer and Lusser, who have identified $[Hg(PPh_2OMe)]^{2+}$ as one of the products resulting from the fragmentation of the mercury-tripod complex $[Hg_2(tripod)](O_3SCF_3)_6$ in MeOH solvent.[3] The dppm containing products observed from this fragmentation are $[Hg_2(\mu\text{-}dppm)_2](O_3CF_3)_4$ and $[Hg(\eta^1\text{-}dppm)_2](O_3CF_3)_2$.[3]

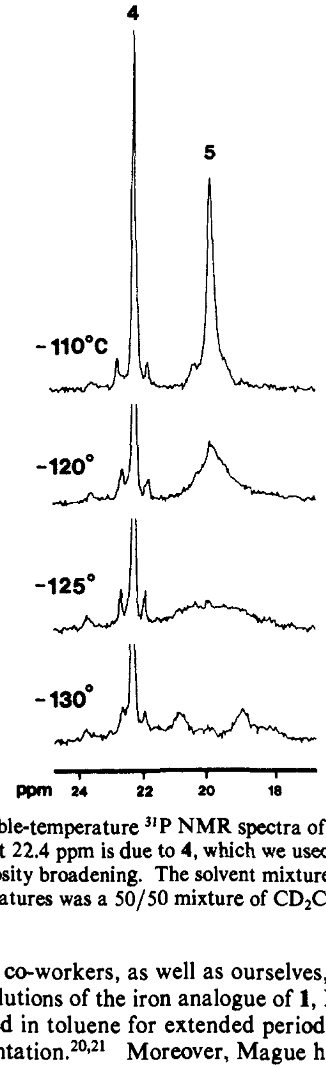
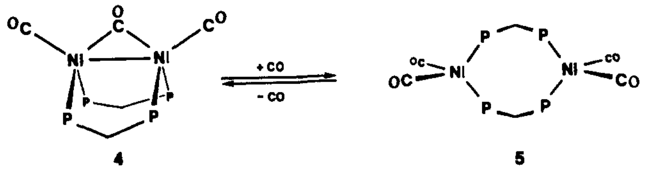


Figure 4. Variable-temperature ^{31}P NMR spectra of $Ni_2(CO)_4(dppm)_2$ (5). The peak at 22.4 ppm is due to 4, which we used as a reference for monitoring viscosity broadening. The solvent mixture used to access the very low temperatures was a 50/50 mixture of $CD_2Cl_2/CHClF_2$ (Freon 12).

Mague and co-workers, as well as ourselves, have noted that oxygen-free solutions of the iron analogue of 1, $Fe(CO)_3$(tripod), can be refluxed in toluene for extended periods with no sign of tripod fragmentation.[20,21] Moreover, Mague has noted that the use of *impure* $Fe_3(CO)_{12}$ in reactions with tripod does cause fragmentation yielding iron–dppm carbonyl dimers.[21] We feel that the presence of either oxygen or various metal impurities (such as nickel metal, which is formed in our refluxing $Ni(CO)_4$/tripod reaction) can lead to tripod fragmentation, and care must thus be taken to avoid such contaminations if intact tripod complexes are desired.

4 readily reacts with 1 equiv of carbon monoxide to quantitatively yield $Ni_2(CO)_4(dppm)_2$ (5). The spectroscopic data on 5 are consistent with the formulation of 5 as a dppm-bridged dimer



4 5

with two terminal carbonyl ligands on each nickel atom. Although the ^{31}P NMR of 5 shows a singlet at room temperature, a variable-temperature NMR study shows that at −110 °C the ^{31}P NMR signal for 5 starts to broaden, with coalescence occurring around −125 °C and what appears to be an AB-type pattern (J_{P-P} = 62 Hz) growing in at −130 °C (Figure 4).

A structure similar to 4 would seem to be unlikely because there does not appear to be enough room for the four carbonyl ligands to lie in the same plane unless there is a substantial twisting of the complex and lengthening of the Ni–Ni distance. We propose that the structure of 5 is similar to that seen for the dppm-bridged

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(17) DeLaet, D. L.; del Rosario, R.; Fanwick, P. E.; Kubiak, C. P. *J. Am. Chem. Soc.* **1987**, *109*, 754.

(18) Holah, D. G.; Hughes, A. N.; Mirza, H. A.; Thompson, J. D. *Inorg. Chim. Acta* **1987**, *126*, L7.

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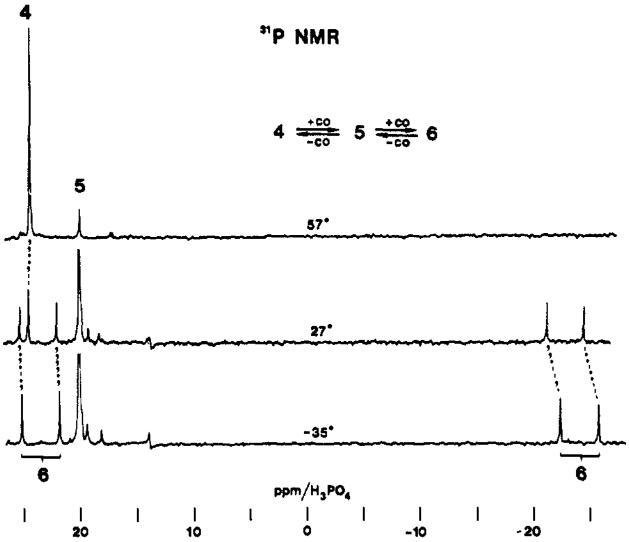


Figure 5. ^{31}P NMR of $Ni_2(CO)_3(dppm)_2$ (4) with carbon monoxide. The peak due to species 5 is truncated in the +27 and −35 °C spectra. The J_{P-P} for the doublets (species 6) is 125 Hz.

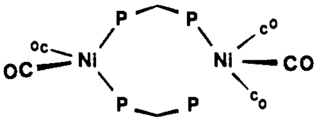
platinum dimer complex $Pt_2(CH_3)_2(dppm)_2$ prepared by Puddephatt and co-workers, which has a Pt–Pt separation of 4.198 (1) Å.[22] Although the $Pt_2(dppm)_2$ dimetallocyclic 8-membered ring system has a twist-boat type of structure with approximate C_2 symmetry, our Ni complex appears to have the higher symmetry C_{2h} twist-chair configuration seen for the related, less bulky bis(dimethylphosphino)methane (dmpm) bridged platinum dimer complex.[22] This conclusion is based on the more symmetrical ^{31}P and ^{13}CO NMR spectra observed for 5. The asymmetry we are starting to freeze out at −130 °C is probably due to a very low-energy distortion of the twist-chair conformation.

The reason 5 adopts the higher symmetry twist-chair configuration is probably tied into the presence of tetrahedral geometry about the Ni(0) atoms, as opposed to the square-planar coordination geometry seen for the Pt(II) compounds. There is, in fact, considerable distortion in the dmpm-bridged platinum dimer from an ideal square-planar environment as indicated by the expanded P–Pt–P angle of 102.9 (2)°.[22] Tetrahedral geometry helps relieve these steric strains and allows our more bulky nickel–dppm dimer to adopt the higher symmetry twist-chair conformation.

5 is a saturated 18-electron compound that should be quite inert toward addition reactions. This quite surprisingly is not the case since 5 also readily reacts with CO to form another carbonyl adduct, 6. The stability of 6 is related to both temperature and carbon monoxide pressure: at low temperatures (<−40 °C) 6 is relatively stable toward CO dissociation; at room temperature 6 must be kept under greater than an atmosphere of CO; and at higher temperatures CO readily dissociates to form 5, and then eventually 4, unless CO pressures greater than several atmospheres are maintained.

The facile CO-based equilibrium between 4, 5, and 6 is illustrated in Figure 5, which shows the variable-temperature ^{31}P NMR after exposing a solution of pure 4 to carbon monoxide. The 27 °C spectrum clearly shows that the signal due to 4 has been dramatically decreased, with 5 becoming the major species and a fair amount of 6 present as the AX doublet–doublet (J_{P-P} = 125 Hz) pattern with a 47 ppm separation. Cooling the solution down to −35 °C causes the equilibrium to shift toward species 6, with 4 now completely gone. Cooling the solution even more causes the equilibrium to shift almost completely to species 6. Rewarming the solution causes the equilibrium to shift back to regenerate species 4 and 5. Warming the solution further to 57 °C causes species 6 to disappear, and the spectrum is now that of mainly 4 with about 10% of 5 present. This equilibrium is reversible and we can cycle the temperatures to regenerate the ^{31}P spectra shown. These temperature effects partially reflect the increasing solubility of CO with decreasing temperature and hence displacement of the equilibrium: 4 → 5 → 6.

One would, on the basis of simple bonding considerations, expect one of the Ni–P bonds to break on the addition of a carbon monoxide molecule to 5 to generate a nickel dicarbonyl/nickel tricarbonyl species such as that shown below. The IR spectrum of 6 certainly appears to be the superposition of $Ni(CO)_2$ and $Ni(CO)_3$ units,[23] and the upfield doublet pattern in the ^{31}P NMR points to the presence of uncoordinated phosphorus atoms. Yet the very simple AX ^{31}P NMR and 1:1 integration ratio for the pattern rules out such an asymmetric species, which should have a rather complicated ABCX pattern. We have taken the ^{31}P NMR of 6 down to −130 °C and have seen no broadening of the ^{31}P NMR signals, which eliminates all but the very lowest energy fluxional processes. We believe that the only species that fits our spectroscopic data for 6 is the mononuclear complex $Ni(CO)_3(\eta^1\text{-dppm})$. This type of structure is consistent with the simple ^{13}CO (doublet, J_{C-P} = 3 Hz) and ^{31}P NMR AX patterns observed. Furthermore, the 125-Hz P–P coupling constant also agrees with that seen for asymmetric or dangling bis(phosphino)methane complexes, which have J_{P-P} couplings ranging from 60 to 130 Hz.[17,24] While we do not know exactly how the addition of CO to 5 proceeds, an intermediate species such as $(CO)_3Ni(\mu\text{-dppm})Ni(\eta^1\text{-dppm})(CO)_2$ shown above would appear to be one distinct possibility.



The anomalous observation that approximately 1 equiv of CO is absorbed by 5 in an uptake experiment (18 °C, $p_{CO} \simeq$ 700 Torr) is a result of the reversible and facile equilibrium established between 5 and 6. Under the uptake experimental conditions, the equilibrium is such that [5] $\simeq$ [6] and, hence, only one CO is absorbed. The same basic argument can also be made for the IR spectrum of the solution, which shows a superposition of $Ni(CO)_2$ and $Ni(CO)_3$ patterns, resulting from a 1:1 mixture of 5 and 6. This is supported by the observations that we have only seen pure 6 in ^{31}P NMR at elevated (>1 bar) CO pressures and/or low temperatures. The thermal sensitivity of 5 (and 6) to carbonyl loss is clearly illustrated by the observation that Nujol mulls of single crystals of 5 grown under CO at 5 °C readily lose CO when placed in the warm beam of an infrared spectrometer, giving rise to the bridging carbonyl complex 4 after a few minutes. The ready and reversible uptake of CO by 4 adds another example to the small list of dimer or cluster systems that are known to exhibit such behavior. Puddephatt, for example, recently reported platinum dimer and trimer compounds that show rapid and reversible CO addition reactions.[25,26]

The facile interconversion of monomeric $Ni(CO)_3(\eta^1\text{-dppm})$ with dimeric $Ni_2(CO)_4(dppm)_2$ is particularly unusual since it has been reported that the reaction of $Ni(CO)_4$ with dppm yields the *chelated* mononuclear species $Ni(CO)_2(dppm)$.[27] Considering the fact that $Ni_2(CO)_4(dppm)_2$ (5) has essentially the same ν_{CO} IR frequencies as that reported for the monomeric $Ni(CO)_2(dppm)$ and an identical elemental analysis, one might be tempted to propose that what Horrocks reported as $Ni(CO)_2(dppm)$ was actually the dimer species 5.[27] Our observation that 5 tends to lose CO rather readily to form the CO-bridged species 4, however, would seem to discount this, as the bridging CO is quite distinctive

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(23) Infrared spectra are included in the supplementary material.

(24) Cf.: (a) Hor, A. T. S. *J. Organomet. Chem.* **1987**, *319*, 213. (b) Ling, S. S. M.; Puddephatt, R. J. *Polyhedron* **1986**, *5*, 1423. (c) Cartwright, S.; Clucas, J. A.; Dawson, R. H.; Foster, D. F.; Harding, M. M.; Smith, A. K. *J. Organomet. Chem.* **1986**, *302*, 403. (d) Grim, S. O.; Mitchell, J. D. *Inorg. Chem.* **1977**, *16*, 1770.

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in the IR and Horrocks makes no mention of any such band in his paper.[27] The possible formation of monomeric Ni(CO)$_2$(dppm) is indirectly supported by the work of Balch and co-workers, which indicates that the reaction of Ni(CO)$_4$ with dppm does not *directly* yield Ni$_2$(CO)$_3$(dppm)$_2$ nor Ni$_2$(CO)$_4$(dppm)$_2$, although they have not worked out the details of the reaction.[16] King has reported that the reaction of Ni(CO)$_4$ with dmpm (dmpm = Me$_2$PCH$_2$PMe$_2$) yields the chelated monomer Ni(CO)$_2$(dmpm) but that reaction of [CpNi(CO)]$_2$ with dmpm yields the binuclear complex Ni$_2$(CO)$_2$(dmpm)$_3$, which should also have a cisoidal dmpm arrangement, but has not been structurally characterized as yet.[28]

A further potential conflict that arises with previously reported work is that Bodner and co-workers have published the ^{13}CO chemical shifts for 116 LNi(CO)$_3$ (L = phosphine, arsine) complexes, one of which is Ni(CO)$_3$(η^1-dppm).[29] On the basis of our observations, the species we are proposing as Ni(CO)$_3$(η^1-dppm) is only stable under CO and/or low temperatures, yet Bodner makes no note of any unusual properties of his nickel system, although very few synthetic details are given. The general procedure reported, however, indicates that the LNi(CO)$_3$ complexes were prepared in situ, which would generate a CO-saturated solution and provide the conditions necessary to produce Ni(CO)$_3$(η^1-dppm). The IR spectrum was checked, but as with our work, the superposition of species **5** and **6** can easily be mistaken for only **6**, particularly if only a quick spectrum of the carbonyl region is run.

Although we have not as yet studied the reactions of dppm with Ni(CO)$_4$, it is clear that more detailed studies are necessary to probe the relationships between Ni(CO)$_2$(dppm), Ni(CO)$_3$(η^1-dppm), and the binuclear species Ni(CO)$_4$(dppm)$_2$ (**5**) and Ni$_2$(CO)$_3$(dppm)$_2$ (**4**). The observation of an unidentified ^{31}P NMR singlet (+19.4 ppm, CH$_2$Cl$_2$) in the general vicinity expected for Ni(CO)$_2$(dppm) (based on that seen for Ni(CO)$_2$(tripod)) indicates that Ni(CO)$_2$(dppm) may indeed be forming but that under our reaction conditions it is not stable with respect to formation of the binuclear species. Further, in view of the interesting base properties shown by the bridging isocyanide ligand in the isoelectronic complex Ni$_2$(μ-CNR)(CNR)$_2$(dppm)$_2$,[11,17] investigations of the reactivity of these carbonyl-bridged Ni dimers can be anticipated.

Experimental Section

Materials and Methods. All manipulations were carried out under an argon or nitrogen inert atmosphere using standard schlenk-line or glovebox techniques. All solvents used in reactions were distilled under nitrogen in the presence of the appropriate O$_2$ and H$_2$O scavenging reagents (e.g., sodium/benzophenone for Et$_2$O, THF, benzene, and hexane; CaH$_2$ for CH$_2$Cl$_2$). Ni(CO)$_4$ was obtained from Strem Chemicals. Tripod (HC(PPh$_2$)$_3$) was prepared by literature methods, and the purity of each batch was confirmed by ^{31}P NMR.[1b] Deuteriated NMR solvents (CD$_2$Cl$_2$ and C$_6$D$_6$) and ^{13}CO (90%) were obtained from the "Service des Molecules Marquees" C.E.A. (France). Elemental analysis was performed by Analytische Laboratorien, 5270 Gummersbach 1 Elbach, West Germany.

NMR spectra were measured on a Bruker WH 90 Fourier transform instrument. Low-temperature runs used an approximately 50:50 mixture of CD$_2$Cl$_2$ (to maintain lock) and CHClF$_2$ (Freon-12), which allowed us to perform low-temperature studies down to −135 °C. Temperature measurements for the NMR experiments are accurate to ±2 °C. Infrared spectra were run on a Perkin-Elmer 597 spectrophotometer.

Synthesis of Ni$_2$(μ-CO)(CO)$_2$(dppm)$_2$ (4). Method A. Two grams (3.5 mmol) of tripod in 40 mL of THF was added by cannula to 0.7 g (3.8 mmol) of Ni(CO)$_4$ in 10 mL of THF in a 100-mL flask equipped with a reflux condenser. On addition of the tripod the solution immediately turned yellow, producing Ni(CO)$_2$(tripod). The solution was heated to reflux and it rapidly turned a dark red-brown. After 24 h of reflux the solution was cooled and vacuum evaporated to half volume. Approximately 40 mL of CH$_2$Cl$_2$ was added to dissolve the yellow precipitate of Ni$_2$(CO)$_3$(dppm)$_2$; the solution was warmed and stirred for an hour and then filtered through Celite to remove any metallic nickel formed. The yellow to yellow-green filtrate was vacuum evaporated to remove the CH$_2$Cl$_2$, producing a yellow precipitate of **4**. This was col-

Table II. Crystallographic Data for Ni$_2$(μ-CO)(CO)$_2$(dppm)$_2$·3C$_6$H$_6$

Crystal Parameters

formula = Ni$_2$P$_4$O$_3$C$_{71}$H$_{62}$
crystal system = orthorhombic
a = 14.015 (8) Å
b = 18.784 (10) Å
c = 22.743 (8) Å
V = 5987 (4) Å^3
d_{calcd} = 1.336 g/mL
crystal size = 0.20 × 0.15 × 0.08 mm
color = orange-yellow (amber)

fw = 1028.58
space group = *Pbcn*
α = 90.00°
β = 90.00°
γ = 90.00°
Z = 4
μ(Mo Kα) = 7.83 cm^{-1}
temp = 22 °C

Data Collection and Structure Refinement

diffractometer = Picker FACS-1
monochromator = graphite cryst
scan speed = 2°/min
octant collected = *hkl*
reflections collected = 3913
no. of parameters refined = 363
R^a = 0.062
quality of fit indicator^c = 1.19
largest final shift/esd = 0.10
absorption correction = no

radiation = Mo Kα
scan method = $\theta/2\theta$
data limits = 3.5° < 2θ < 45°
Friedel pairs collected = no
unique data $F_o^2 > 3\sigma(F_o)^2$ = 1237
data/parameter ratio = 3.4^d
R^{wb} = 0.086
largest final Fourier peak = 0.6 e/Å^3
least-squares method = block diagonal

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma(|F_o|)$. [c] Quality of fit = $[\sum w(|F_o| - |F_c|)^2/(N_{obsd} - N_{parameters})]^{1/2}$. [d] The data/parameter ratio is very low due to the small crystal, which did not give a high-quality data set.

Table III. Positional Parameters for Ni$_2$(μ-CO)(CO)$_2$(dppm)$_2$·3C$_6$H$_6$[a]

atom	x	y	z	B, Å^2
Ni1	0.09020 (14)	0.84576 (9)	0.26356 (8)	4.53 (9)
P1	0.4245 (3)	0.27280 (20)	0.33944 (17)	4.3 (2)
P2	0.3682 (3)	0.28300 (20)	0.18544 (17)	4.0 (2)
C1	0.4249 (10)	0.3169 (8)	0.4121 (5)	4.7 (8)
C2	0.4302 (11)	0.3899 (8)	0.4140 (7)	6.3 (10)
C3	0.4315 (12)	0.4231 (10)	0.4703 (7)	7.7 (11)
C4	0.0751 (12)	0.1201 (10)	0.0216 (6)	7.5 (11)
C5	0.0800 (14)	0.1930 (10)	0.0162 (7)	7.9 (11)
C6	0.4146 (11)	0.2730 (9)	0.4620 (6)	6.6 (9)
C7	0.3369 (10)	0.2044 (7)	0.3497 (5)	4.2 (8)
C8	0.2432 (12)	0.2245 (9)	0.3441 (6)	6.6 (9)
C9	0.1677 (14)	0.1713 (10)	0.3510 (7)	8.4 (12)
C10	0.1894 (12)	0.1019 (10)	0.3596 (7)	7.5 (11)
C11	0.2840 (13)	0.0798 (9)	0.3656 (7)	8.1 (11)
C12	0.3631 (12)	0.1340 (7)	0.3585 (7)	6.3 (10)
C13	0.3376 (10)	0.3349 (7)	0.1207 (6)	4.3 (8)
C14	0.3254 (10)	0.4095 (8)	0.1283 (7)	5.7 (9)
C15	0.2951 (12)	0.4509 (9)	0.0802 (7)	7.0 (10)
C16	0.2825 (11)	0.4199 (9)	0.0251 (7)	6.2 (10)
C17	0.2959 (13)	0.3476 (10)	0.0179 (7)	7.9 (12)
C18	0.3239 (10)	0.3041 (8)	0.0661 (6)	5.1 (8)
C19	0.2679 (10)	0.2235 (8)	0.1882 (5)	4.8 (8)
C20	0.1739 (11)	0.2538 (8)	0.1862 (7)	7.1 (10)
C21	0.0890 (12)	0.2133 (10)	0.1917 (7)	8.7 (12)
C22	0.1056 (13)	0.1393 (8)	0.1980 (6)	7.4 (11)
C23	0.1891 (12)	0.1085 (8)	0.1987 (6)	7.2 (10)
C24	0.2728 (12)	0.1509 (8)	0.1953 (6)	6.1 (10)
C25	0.4609 (9)	0.2229 (7)	0.1594 (6)	4.1 (7)
C26	0.50000	0.4186 (9)	0.25000	6.8 (15)
C27	0.3079 (13)	0.4004 (8)	0.2826 (7)	7.7 (11)
O1	0.50000	0.4770 (8)	0.25000	13.8 (17)
O2	0.2421 (11)	0.4313 (7)	0.2932 (7)	13.4 (10)
C28	−0.0075 (16)	0.3814 (11)	0.4490 (10)	11.6 (16)
C29	−0.0065 (19)	0.4107 (15)	0.5040 (10)	12.2 (17)
C30	0.4339 (15)	0.0846 (12)	0.0357 (10)	12.0 (16)
C31	0.3421 (18)	0.1061 (11)	0.0152 (10)	11.7 (17)
C32	0.1615 (14)	0.3653 (12)	0.4619 (11)	11.7 (16)
C33	0.0824 (17)	0.3533 (13)	0.4255 (12)	14.7 (19)
C34	0.00000	0.4127 (18)	0.25000	15.3 (34)
C35	0.053 (3)	0.4477 (21)	0.2018 (14)	26.5 (34)
C36	0.0261 (23)	0.5156 (16)	0.2079 (15)	20.6 (29)
C37	0.00000	0.5357 (23)	0.25000	15.7 (32)

[a] Numbers in parentheses represent esd's for the last digit listed. Anisotropically refined atoms are given an isotropically equivalent thermal parameter that is the arithmetic mean of the principal axes of the thermal elipsoids.

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lected and washed with cold THF to give 1.0 g (38% yield based on tripod) of crude **4**. **4** is very soluble in CH_2Cl_2; moderately soluble in benzene, acetone, and toluene; only sparing soluble in THF; and insoluble in nonpolar organic solvents such as pentane or hexane. **4** can be readily recrystallized by slow evaporation from a $CH_2Cl_2/C_6H_6/THF$ mixture. **4** is air-stable in the solid-state for days to weeks, but solutions gradually decompose to unidentified green solutions and should be handled under an inert atmosphere.

Method B. Dissolve $Ni(CO)_2$(tripod) (for literature preparation, see ref 2) in a 50:50 mixture of THF and benzene and let stand in a flask with a rubber septum that has several needle holes punched into it to allow a very slow seepage of oxygen into the flask. Well-formed single crystals of **4** will begin growing from the amber solution after about 2 weeks and will continue to grow until most of the starting material is used up (1-2 months).

Spectroscopic data on $Ni_2(\mu\text{-}CO)(CO)_2(dppm)_2$ (**4**): color, yellow; IR (ν_{CO}, cm^{-1}, CH_2Cl_2) 1963 (s, sh), 1942 (vs), 1770 (m); ^1H NMR (ppm, TMS, CH_2Cl_2) 2.6, 3.4 (P-CH_2-P, multiplets, 2 H each), 6.9, 7.0, and 7.3 (Ph, multiplets, 40 H); ^{31}P NMR (ppm, H_3PO_4, CH_2Cl_2) 24.2 (s) (57 to -135 °C); ^{13}C carbonyl NMR (ppm, TMS, 50-80% ^{13}CO enriched, CH_2Cl_2) 200 (s), 243 (quint, J_{P-C} = 7 Hz) (57 to -135 °C). Anal. Calcd for $C_{53}H_{44}Ni_2O_3P_4$ (**4**): C, 64.80; H, 4.52; Ni, 11.66; P, 12.54. Found: C, 64.80; H, 4.52; Ni, 11.66; P, 12.53.

Preparation of $Ni_2(CO)_4(dppm)_2$ (5) and $Ni(CO)_3(dppm)$ (6). Addition of CO to **4** will produce a mixture of **5** and **6**. The ratio of **4**:**5**:**6** is dependent on the temperature and pressure of carbon monoxide. Higher temperatures and lower pressures of CO favor **4**, while the opposite conditions favor species **6**. Crystals of **5** can be grown from CO-saturated CH_2Cl_2 solutions evaporated at 5 °C using a slightly pressurized flow of carbon monoxide. The crystals, however, readily lose both CH_2Cl_2 molecules of crystallization and carbon monoxide at temperatures much above 20 °C. Species **6** has only been observed spectroscopically.

Spectroscopic data on $Ni_2(CO)_4(dppm)_2$ (**5**): color, very pale yellow; IR (ν_{CO}, cm^{-1}, CH_2Cl_2) 2010 (vs), 1995 (vs, sh), 1948 (s, sh), 1933 (vs); ^{31}P NMR (ppm, H_3PO_4, CH_2Cl_2) 19.6 (s) (25 °C); ^{13}C carbonyl NMR (ppm, TMS, 50-80% ^{13}CO enriched, CH_2Cl_2) 196 (s) (25 °C).

Spectroscopic data on $Ni(CO)_3(\eta^1\text{-}dppm)$ (**6**): color, colorless; IR (ν_{CO}, cm^{-1}, CH_2Cl_2) 2070 (s), 1995 (vs), 1940 (m); ^{31}P NMR (ppm, H_3PO_4, CH_2Cl_2) doublet-doublet centered at +23.4 and -24.2 (J_{P-P} = 125 Hz).

X-ray Structure Determination on $Ni_2(\mu\text{-}CO)(CO)_2(dppm)_2$ (4). Single crystals of **4** were obtained from the NMR tube of $Ni(CO)_2$(tripod) in THF/C_6D_6 after several weeks of standing. A yellow crystal of **4** measuring 0.20 × 0.15 × 0.08 mm was mounted in a glass capillary. Preliminary Weisenberg and precession photographs established the unit cell constants and crystal class (orthorhombic). Data were collected on a Picker FACS-1 computer-controlled diffractometer at room temperature using Mo Kα radiation. Final unit cell constants based on 25 computer-centered reflections are a = 14.015 (2) Å, b = 18.784 (5) Å, c = 22.743 (8) Å, V = 5987 (4) Å^3, and Z = 4.

A total of 3913 reflections were collected and the space group *Pbcn* was uniquely established from systematic absences. The structure was solved by Patterson and direct methods techniques and refined by using 1237 independent reflections with $F_o^2 > 3\sigma(F_o)^2$. The $Ni_2(\mu\text{-}CO)(CO)_2(dppm)_2$ molecule sits on a 2-fold crystallographic axis passing through the bridging carbonyl group. There are three solvent molecules of benzene per nickel dimer. The final discrepancy indices are R = 0.062 and R_w = 0.086 with a GOF of 1.19. Crystal parameters, data collection, and structure refinement data are summarized in Table II. A list of fractional coordinates is listed in Table III. Tables of anisotropic thermal parameters and F_o/F_c are included in the supplementary material.

The data to parameter ratio (3.4) is quite a bit smaller than we would like due to the small size of the crystal and the fact that it did not diffract particularly well. There was a monoclinic modification of the crystals that produced much larger crystals, but we were unable to solve the monoclinic structure, even after solving the orthorhombic structure.

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Registry No. **1**, 75790-05-5; **4**, 106251-27-8; **4**·$3C_6H_6$, 112965-96-5; **5**, 112896-40-9; **6**, 62945-83-9; $Ni(CO)_4$, 13463-39-3; Ni, 7740-02-0.

Supplementary Material Available: IR spectra of the carbonyl regions for **4**, **5**, and **5**/**6**, tables of thermal parameters, and a full listing of bond distances and angles (5 pages); tables of observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

Evidence for the Intermediacy of Chromium-Ketene Complexes in the Synthesis of β-Lactams by the Photolytic Reaction of Chromium-Carbene Complexes with Imines. Use in Amino Acid Synthesis

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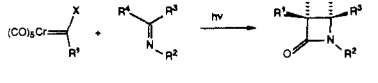
Abstract: Photolysis of chromium-carbene complexes in the presence of nucleophiles gives ketene-derived products. This observation, in conjunction with the stereoselectivity observed in the photolytic reactions of chromium-carbene complexes with imines to produce β-lactams, suggests the intermediacy of photolytically generated, metal-coordinated ketenes. Photolysis of chromium-carbene complexes containing a chiral, optically active amino alcohol group produced lactones in high yield and high diastereoselectivity. These lactones are convertible to optically active amino acids.

A new synthetic approach to β-lactams involving the photolytic reaction of heteroatom-stabilized ("Fischer") chromium-carbene complexes with imines was recently developed in these laboratories (eq 1).[1-4] The process is quite general and tolerates wide variations in the structure of both the carbene and the imine. The reactions proceed in high yield under very mild conditions



(1)

(R's = Me, Ph, H, X = MeO, NR$_2$)

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