A Broadly Applicable Strategy for Entry into Homogeneous Nickel(0) Catalysts from Air-Stable Nickel(II) Complexes

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ABSTRACT: A series of air-stable nickel complexes of the form L₂Ni(aryl)X (L = monodentate phosphine, X = Cl, Br) and LNi(aryl)X (L = bis-phosphine) have been synthesized and are presented as a library of precatalysts suitable for a wide variety of nickel-catalyzed transformations. These complexes are easily synthesized from low-cost NiCl₂·6H₂O or NiBr₂·3H₂O and the desired ligand followed by addition of 1 equiv of Grignard reagent. A selection of these complexes were characterized by single-crystal X-ray diffraction, and an analysis of their structural features is provided. A case study of their use as precatalysts for the nickel-catalyzed carbonyl-ene reaction is presented, showing superior reactivity in comparison to reactions using Ni(cod)₂. Furthermore, as the precatalysts are all stable to air, no glovebox or inert-atmosphere techniques are required to make use of these complexes for nickel-catalyzed reactions.

INTRODUCTION

Homogeneous nickel catalysis has continued to develop in recent years as a powerful set of tools for the construction of a wide variety of carbon–carbon and carbon–heteroatom bonds.† Nickel, a base metal, is a low-cost, versatile, and attractive metal for use in catalytic transformations. Arguably the greatest barrier to the wider adoption of homogeneous nickel catalysis for synthesis, however, is the difficulty and cost of synthesizing and handling nickel(0) sources and the phosphines often used in conjunction with such complexes. It is for this reason we aim to further develop nickel(II)-based precatalysts, as this would greatly increase the accessibility of homogeneous nickel catalysis in both academic as well as industrial settings.

Ideally, these precatalysts would (1) be indefinitely air stable, (2) have a low molecular weight, (3) be highly active, (4) be simple to synthesize from low-cost materials, (5) be readily activated under a variety of conditions without producing interfering byproducts of activation, and (6) be applicable to virtually any nickel-catalyzed transformation. Precatalysts possessing many or all of these qualities would greatly add to the value of new as well as previously established nickel-catalyzed transformations.

Although nickel metal itself is extremely low in cost (~$15 USD/kg at commodity prices), the cost of nickel(0) sources such as Ni(cod)₂ (cod = 1,5-cyclooctadiene) easily exceeds $20000 USD/kg, which often weakens the economic argument for using nickel in catalytic transformations. Indeed, Ni(cod)₂ is only marginally less expensive than comparable palladium(0) sources such as Pd₃(db)₆ (dba = dibenzylideneacetone) on a mole-for-mole basis, despite the fact that palladium metal is far more expensive than nickel metal.² Taken in conjunction with the fact that a high catalyst loading of nickel is often required (5–20 mol %), there is little economic incentive to use nickel in place of precious metals such as palladium unless cheaper sources of nickel can be used. Regardless of cost and ease of use issues, however, any comparison between nickel and precious metals (particularly palladium) should recognize that nickel has demonstrated valuable and unique reactivity and behavior, which enables an entirely different set of chemical transformations.³

The use of precatalysts in transition-metal catalysis is not a new idea: indeed, Pd(OAc)₂ has been in use as a precursor to Pd(0) species for close to 50 years,³ though the concept of the single-component, discrete precatalyst is a somewhat newer development.⁴ Several groups (Nolan,⁵ Buchwald,⁶ Organ,⁷ and others) have greatly advanced the ubiquity of precatalysts in organic synthesis, with much of the effort focused on palladium catalysts for cross couplings, amination, and related transformations.⁸ Likewise, though by far less established than those for palladium-catalyzed reactions, single-component nickel precatalysts are not new, with the most frequently employed being complexes such as (PPh₃)₂NiCl₂.⁹ Though air stable, these precatalysts are usually limited to activation by nucleophilic organometallic reagents, and as such, they must often be preactivated by addition of an exogenous reductant.¹⁰ Such a strategy has been shown to be effective in many instances but is neither an ideal nor a universal solution.

Complexes such as trans-(PPh₃)₂Ni(1-naphthyl)Cl have been known to be air-stable since 1960, when they were first reported by Chatt and Shaw,¹¹ but these complexes were not...
utilized in catalytic transformations until many years later. Relatively few phosphine ligands have been used to prepare such complexes for use in catalysis, although several new types of nickel precatalysts with varying degrees of air stability have also been developed in the past few years.

During the development of trans-(PPh₃)₂Ni(o-toly)Cl for use in the coupling reaction of benzyl chlorides with alkynes, it became apparent that such complexes could be used for numerous nickel-catalyzed transformations, since these precatalysts can be activated by nucleophilic reagents (RMgX, RZnX, R₃B, R₅SiH—by a transmetallation/reductive elimination sequence) as well as electrophilic reagents (R₂SiO Tf—by a Lewis acid induced Ni to Ni transmetallation followed by reductive elimination of a biaryl). Members of this class have been shown to possess significantly enhanced catalytic activity in comparison to the combination of Ni(cod)₂ and the corresponding phosphine ligand due to the absence of cod, which is known to hinder catalysis in some instances.

### RESULTS AND DISCUSSION

Synthesis of the precatalyst complexes is straightforward (see Scheme 1): NiCl₂·6H₂O and the desired mono- or bidentate phosphine are combined in ethanol and briefly refluxed, after which the L₂NiCl₂ complex is isolated by a simple vacuum filtration method. In both instances, the addition of another 1 equiv of o-tolylmagnesium chloride takes place very readily (which lowers the yield and purity of the isolated product) and neither complex is very stable to methanol, leading to a loss of yield during workup and purification. In both instances, however, changing the aryl group to a mesityl group solved this problem, allowing isolation of cis-[dppp]Ni(2-mesityl)Br (13) and trans-[dppp]Ni(2-mesityl)Br (14). It should be noted, however, that the complexes containing the o-tolyl ligand can be synthesized by metathesis starting from trans-(PPh₃)₂Ni(o-toly)Cl (1), indicating they are indeed stable complexes.

Unfortunately, the switch from o-tolyl to 2-mesityl did not enable isolation of a stable complex in one instance: PMe₂Ph. Neither the o-tolyl nor the 2-mesityl complexes were stable under ambient conditions or in the presence of alcohols. Because PMe₂Ph represents the least sterically demanding phosphine used in this study, it is perhaps unsurprising that its complex is in turn the most sensitive to nucleophilic attack by water or alcohols, since nickel is less shielded. As before, increasing the steric hindrance around nickel provided the solution. Reaction of trans-(PMe₂Ph)₂NiBr₂ with 2,4,6-trisopropylphenylmagnesium bromide gave trans-(PMe₂Ph)₃Ni(2,4,6-trisopropylphenyl)Br (8) in 83% yield. This complex, in stark contrast to the corresponding o-tolyl and 2-mesityl complexes, demonstrates absolutely no air or water sensitivity.

However, due to the concern that activation of this precatalyst may be slow because of the extreme hindrance provided by the isopropyl groups at the 2- and 6-positions of the aryl ring, a precatalyst incorporating a 2,6-dimethoxyphenyl substituent (9) was also prepared and found to be air stable. As the numerous entries in Table 1 demonstrate, complexes of this type can be made from a wide range of phosphines, including electron-rich and electron-poor as well as sterically demanding and undemanding phosphines. However, a number of phosphines were not able to be successfully incorporated into these types of complexes. Those ligands fall into two categories: electron-poor and sterically hindered (P(4-F-... )
C_{6}H_{4})_{3}, P(o-tol)_3, and P(o-anis)_3) and extremely sterically hindered phosphines, regardless of their electronic nature (P(t-Bu)_3, \(9,9\)-dimethyl-9H-xanthene-4,5-diylibis(di-tert-butylphosphine)), and 1,2-bis((di-tert-butylphosphino)methyl)-benzene). In all instances the L_{2}NiX_2 or LNiX_2 complexes did not form, precluding attempts to synthesize the corresponding arylnickel complexes by this synthetic route. Although our principal interest in these complexes is their catalytic activity, it is also important to understand their structural features, geometry, and bonding, as this may afford deeper insight that would enable further development of new complexes, types of precatalysts, or alternative modes of activation.

The complexes strongly favor a square-planar arrangement, and whether the two phosphorus atoms are in a cis or trans

Table 1. Nickel Phosphine Complexes Synthesized

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“Abbreviations: dppe, 1,2-bis(diphenylphosphino)ethane; dppp, 1,3-bis(diphenylphosphino)propane; dppb, 1,4-bis(diphenylphosphino)butane; BINAP, 2,2’-bis(diphenylphosphino)-1,1’-binaphthyl; dppf, 1,1’-bis(diphenylphosphino)ferrocene; dcpf, 1,1’-bis(dicyclohexylphosphino)ferrocene; Xantphos, 9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene; pyphos, 2-[2-(diphenylphosphino)ethyl]pyridine.

Figure 1. Complexes analyzed by single-crystal X-ray diffraction. Thermal ellipsoids are drawn at the 50% probability level, and hydrogen atoms are not included. Disorder of the o-tolyl ligand (6, 15, 18, 19) and solvent molecules of crystallization (6, 15, 17, 18) are not shown.
Table 2. Screening of the Ni-Catalyzed Carbonyl-Ene Reaction

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<th>entry</th>
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*See the Supporting Information for complete data for all complexes. Reactions were carried out on a 0.50 mmol scale with 20 mol % of catalyst and run for 48 h. Yields determined by gas chromatography calibrated against an internal standard of n-dodecane.

Organometallics

A comprehensive screen of precatalysts 1—19 was carried out to demonstrate the ease with which screening of ligands can be accomplished (abbreviated results are shown in Table 2; see the Supporting Information for complete data). The use of these single-component, air-stable precatalysts reduces the effort involved to an exercise which can be carried out on the benchtop with no exclusion of air during setup of the reactions. This approach, while convenient, may however not be applicable in all instances, as it is necessary to have already synthesized the desired precatalysts. For researchers frequently

arrangement at nickel is readily discerned from inspection of each complex’s 31P NMR spectrum. Complexes derived from monodentate phosphines were universally found to adopt a trans geometry, as indicated by the presence of only one singlet in the 31P NMR spectrum. This arrangement presumably results from the minimization of steric interaction between the ligands on nickel, and the magnitude of the steric repulsion is evidently large enough to overwhelm any thermodynamic trans effects that might favor a cis arrangement. Conversely, complexes derived from bidentate phosphines were more often observed to adopt a cis arrangement, but several counterexamples were also seen. The preferred arrangement appears to depend on the bite angle of the ligand, its rigidity, and the identity of the substituents on phosphorus.

For example, the complex derived from dcpf (16) exists only as the cis, square planar isomer in solution, whereas the closely related dcpp (17) adopts a distorted trans, square planar geometry, as illustrated in its single-crystal X-ray structure and in its 31P NMR spectrum. In this instance, the change from phenyl groups to cyclohexyl groups on phosphorus is enough to alter the preferred geometry, despite the fact that both complexes are built on the same ferrocene scaffold.

A selection of these precatalysts have been characterized by single-crystal X-ray diffraction (Figure 1). Crystal structures were determined following established procedures, and complete details are given in the Supporting Information. Complexes derived from PhP₃ and PMe₃Ph both adopt nearly ideal trans, square planar structures and are, for the most part, structurally unremarkable. Complex 15 (derived from (S)-BINAP) adopts a nearly ideal square planar structure with a cis arrangement, yielding a dihedral angle of 73.24° between the two naphthalene rings of BINAP. The most interesting feature of this complex, though, is the fact that it forms diastereomers due to the two possible arrangements of the o-tolyl group. These diastereomers are both crystallographically and spectroscopically (1H and 31P NMR) observable, suggesting that interconversion is either slow or does not take place at any appreciable rate near room temperature.

The complex derived from dcpp (17) is another interesting case: its 31P NMR spectrum exhibits one singlet, despite the fact that it is a bidentate phosphine. XRD analysis showed a geometry at nickel that is best described as square planar, but with significant distortion toward tetrahedral. For example, the P(1)−Ni−P(2) bond angle is ca. 145°, well shy of the ideal 180°. However, the P(1)−Ni−Cl and P(2)−Ni−Cl bond angles are 91.264(13) and 91.642(13)°, very close to the ideal 90° for a square plane. Because of this, it is appropriate to describe the two phosphorus atoms as trans to one another.

Complex 18 (derived from Xantphos) adopts a distorted-square-pyramidal geometry in the solid state. The oxygen atom of the ligand occupies the apical position and the two phosphorus atoms are in equatorial positions trans to each other. In solution, two isomers are observed by 1H and 31P NMR, the second perhaps being the true square-planar isomer, without oxygen coordinated at nickel.

Pyphos (19), being an unsymmetrical, bidentate ligand, can form at least two structural isomers—chloride could be trans to either phosphorus or to nitrogen. The 31P NMR spectrum shows only one, sharp singlet, which suggests that one isomer is dominant in solution. Single-crystal X-ray diffraction analysis showed 19 to adopt a square-planar structure with chlorine trans to phosphorus. This geometrical arrangement presumably indicates that the thermodynamic trans effect dominates the ground-state conformation, rather than any potential steric interaction between the diphenylphosphino moiety and the o-tolyl ligand.

To demonstrate the utility and advantages these precatalysts present over other means of entry into nickel(0), we have used the nickel-catalyzed carbonyl-ene reaction, which couples a terminal alkene (or ethylene), an aldehyde, and a silyl triflate to form allylic or homoallylic silyl ethers (Table 2). Preliminary experiments demonstrated that catalysts 3 and 1 were indeed catalytically competent and provided the desired allylic (20) and homoallylic (21) products, respectively. In both instances, the selectivity and yields were observed to be comparable to those of reactions using Ni(cod)₂. However, the rate was observed to be higher than when cod is present—following studies demonstrated that the reaction reaches completion in ca. 18 h, rather than the 36–48 h required when using Ni(cod)₂ as the nickel source.
involved in screening of nickel-catalyzed reactions, however, such an approach could be valuable.

**CONCLUSION**

In summary, we have synthesized and characterized 19 air-stable Ni(II) complexes derived from a range of mono- and bidentate phosphine ligands commonly used in synthesis. These complexes are accessed from low-cost NiCl₂·6H₂O rather than from an expensive and air-sensitive Ni(0) source such as Ni(cod)₂. These complexes can function as precatalysts for a range of nickel-catalyzed reactions, as they are readily converted to Ni(0) phosphine complexes by treatment with reagents such as RMgX, RZnX, R₂B, RLi, R₂SiH, and R₂SiOTf among others, allowing their convenient use in Ni(0)-catalyzed reactions. Many of these reactions, which previously employed Ni(cod)₂ as the Ni(0) source and thus required the use of a reducing agent, could now be accomplished directly using Ni(0) without the need for a reducing agent.

**EXPERIMENTAL SECTION**

**General Considerations.** Dichloromethane, THF, and acetoni-trile were degassed by sparging with nitrogen and dried by passage through a column of activated alumina. Ethanol (200 proof, <0.1% water) and n-butanol (99.9%) were roughly degassed by sparging with nitrogen and were not further dried prior to use. Methanol (>99.8%, <0.1% water) was used as received. Manipulation of all air-sensitive reagents was performed under an atmosphere of dry nitrogen or argon (99.99%), and stored at −20 °C. Dichloromethane, THF, and acetone were degassed and dried by passage through a column of activated alumina. Ether (202 MHz with 1H decoupling). Chemical shifts (1H and 13C) are referenced to the residual solvent peak (1H, CDCl₃ 7.26 ppm, C₆D₆ δ = 0.00 ppm) and were determined on a Varian Mercury spectrometer. 1H NMR spectra were obtained at 300 MHz while 13C NMR spectra were recorded at 75 MHz. The following designations are used to describe multiplicities: s (singlet), d (doublet), t (triplet), q (quartet), br (broad), app (apparent).

**General Procedure.** L₈NiX₂. NiCl₂·6H₂O or NiBr₂·3H₂O, EtOH, and a magnetic stir bar were placed in a round-bottom flask. The flask was sealed with a rubber septum, the solution was sparged with nitrogen for 15 min, the septum was removed, and then the phosphine was added in one portion. The flask was fitted with a reflux condenser, and the mixture was heated to 80 °C for 30 min and then cooled to room temperature. Once cool, the flask was chilled to 0 °C for 10 min, after which the solid was collected by vacuum filtration and washed twice with ethanol (and twice with ether in some instances). Drying under vacuum yielded the product.

<L₈Ni(aryl)X> L₈NiX₂ was placed in an oven-dried round-bottom flask containing a magnetic stir bar. Solvent (THF or CH₂Cl₂) was added, the solution was cooled to 0 °C with an ice bath, and Grignard reagent was added dropwise with vigorous stirring. The solution was stirred for 15 min at 0 °C, after which the stir bar was removed and the solution was evaporated to dryness under reduced pressure. MeOH was added, and the mixture was sonicated until a uniform suspension was obtained (approximately 5 min). After the suspension was cooled to 0 °C, the precipitate was collected by vacuum filtration, washed with two portions of cold MeOH, and dried under high vacuum to yield the complex.

**Representative Syntheses.** (PMePh₂)₃NiCl₂. NiCl₂·6H₂O (17.42 mmol, 4.141 g), EtOH (55 mL), and a magnetic stir bar were placed in a 100 mL round-bottom flask. The flask was sealed with a rubber septum, the solution was sparged with nitrogen for 15 min, and then PPh₃·Me (38.32 mmol, 7.672 g, 7.13 mL) was added portionwise over 5 min. The flask was equipped with a reflux condenser, and the mixture was heated to 80 °C for 30 min then cooled to room temperature. Once cool, the flask was chilled to 0 °C for 10 min, after which the solid was collected by vacuum filtration and washed twice with ethanol (5 mL). Drying under vacuum yielded S7 (9.111 g, 99%) as a deep maroon, crystalline solid.

**General Procedure.** (PMePh₂)₃NiCl₂ (8.29 mmol, 4.394 g) was placed in an oven-dried, 100 mL round-bottom flask containing a magnetic stir bar. THF (55 mL) was added, the solution was cooled to 0 °C with an ice bath, and o-tolylmagnesium chloride (8.29 mmol, 0.856 M in THF, 9.68 mL) was added dropwise with vigorous stirring. Near the end of the addition, the solution began to turn orange. The solution was stirred for 15 min at 0 °C, after which the stir bar was removed and the solution was evaporated to dryness under reduced pressure. MeOH (25 mL) was added, and the mixture was sonicated until a uniform suspension was obtained (approximately 2 min). After the suspension was cooled to 0 °C, the bright yellow precipitate was collected by vacuum filtration, washed with two portions of cold MeOH (10 mL), and dried under high vacuum to yield 7 (3.940 g, 81%) as a fine, bright yellow powder. Mp: 139–140 °C. Anal. Calcd for C₁₃H₁₆NiP₂: C, 67.67; H, 5.68. Found: C, 66.19; H, 5.98. 1H NMR (500 MHz, C₆D₆, δ) 7.84 (br s, 4H), 7.62 (br s, 4H), 7.12–6.94 (m, 13H), 6.72–6.64 (m, 1H), 6.64–6.53 (m, 2H), 2.75 (s, 3H), 1.08 (s, 6H). 31P{1H} NMR (121 MHz, C₆D₆, δ) 140.3 (br s, 3H) ppm. L₈Ni(aryl)X L₈NiX₂ was placed in an oven-dried round-bottom flask containing a magnetic stir bar. Solvent (THF or CH₂Cl₂) was added, the solution was cooled to 0 °C with an ice bath, and Grignard reagent was added dropwise with vigorous stirring. The solution was stirred for 15 min at 0 °C, after which the stir bar was removed and the solution was evaporated to dryness under reduced pressure. MeOH (20 mL) was added, and the mixture was sonicated until a uniform suspension was obtained (approximately 5 min). After the suspension was cooled to 0 °C, the...
yellow precipitate was collected by vacuum filtration, washed with two portions of cold MeOH (5 mL), and dried under high vacuum to yield 12 (1.92 g, 84%) as a fine, bright yellow powder. Mp: 190–192 °C dec. Anal. Calcld for C_{33}H_{31}ClNiP_2: C, 67.90; H, 5.35. Found: C, 7.3 Hz, 4H), 7.77 (dd, J = 9.2, 7.1, 1.8 Hz, 2H), 7.62–7.41 (m, 9H), 7.31 (t, J = 7.1 Hz, 1H), 7.20 (dt, J = 8.4, 4.7 Hz, 1H), 7.07 (dd, J = 7.7, 2.6 Hz, 2H), 6.71 (dd, J = 10.8, 7.6 Hz, 2H), 6.59 (dd, J = 6.0, 2.9 Hz, 2H), 6.45–6.39 (m, 1H), 2.58–2.34 (m, 2H), 2.34–2.09 (m, 4H), 1.60 (tt, J = 14.4, 11.7, 6.7 Hz, 1H). ^31P(^1)H NMR (121 MHz, CDCl_3): δ: 53.09 (d, J = 17.9 Hz), 35.78 (d, J = 17.8 Hz). ^13C(^1)H NMR (126 MHz, CDCl_3): δ: 158.03 (d, J = 86.1, 38.5 Hz), 143.71 (t, J = 2.0 Hz), 136.17 (dd, J = 3.1, 1.7 Hz), 134.97 (d, J = 11.2 Hz), 134.08 (d, J = 11.2 Hz), 133.14 (d, J = 10.3 Hz), 132.20 (d, J = 8.4 Hz), 131.92 (d, J = 2.6 Hz), 131.66 (d, J = 1.5 Hz), 131.28 (d, J = 2.1 Hz), 130.87 (dd, J = 47.8, 0.6 Hz), 130.73 (d, J = 2.3 Hz), 130.39 (dd, J = 31.9, 0.8 Hz), 130.35 (d, J = 2.7 Hz), 129.72 (dd, J = 56.0, 5.0 Hz), 129.38 (d, J = 9.2 Hz), 129.28 (d, J = 10.5 Hz), 129.02 (dd, J = 6.3, 2.4 Hz), 128.84 (d, J = 9.4 Hz), 127.94 (d, J = 10.1 Hz), 123.49 (dd, J = 6.3, 1.7 Hz), 122.71 (t, J = 1.2 Hz), 29.34 (dd, J = 27.7, 21.7 Hz), 25.50 (q, J = 17.7 Hz), 22.22 (dd, J = 26.0, 11.4 Hz). IR (ATR, cm⁻¹): 3051 (w), 1651 (w), 1434 (m), 1421 (w), 1098 (m), 1026 (m), 1012 (w), 999 (w), 873 (w), 817 (m), 749 m), 742 (s), 708 (m), 692 (s), 679 (m), 652 (m).

### ASSOCIATED INFORMATION

#### Supporting Information

Text, figures, tables, and CIF files giving experimental procedures and spectral data for complexes 1–19, X-ray crystallographic data for complexes 6, 9, 15, 17, 18, 19, a description of single-crystal X-ray diffraction experiments, and full reaction screening information and procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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### REFERENCES

7. Palladium metal is more than 1500 times more expensive than nickel metal, yet the cost of Ni(cod₂) is only ca. 50% less than Pd₂(dbas), as a result of the reagents required for their synthesis, yield of the reaction, and cost of purification.


(b) For a detailed report examining the role of dba in zerovalent palladium catalysis, see: Amatore, C.; Jutand, A.; Khalil, F.; M’Barki, M. A.; Mottier, L. Organometallics 1993, 12, 3168–3178.

(18) The change from chloride to bromide is merely for convenience, since 2-mesitylmagnesium bromide is commercially available, while the chloride is not. The identity of the halogen does not appear to alter the behavior of the complexes as precatalysts.

(19) This particular Grignard reagent was selected for the isopropyl groups at the 2- and 6-positions, with the isopropyl group in the 4-position not expected to play a role in the complex’s stability. This reagent is commercially available as a 0.5 M solution in THF.

(20) It is known, for example, that P(t-Bu)3 reacts with NiBr2 in ethanol to form \([\text{P(t-Bu)}_3\text{NiBr}_3]^-\cdot\text{[HP(t-Bu)}_3]^-\). See: Alyea, E. C.; Costin, A.; Ferguson, G.; Fey, G. T.; Goel, R. G.; Restivo, R. J. J. Chem. Soc., Dalton Trans. 1975, 1294–1298.


(23) This deviation in geometry is also likely to be the reason this complex is red, as opposed to the normal bright yellow.


(25) Complex 7 is somewhat soluble in methanol, causing the lower yield in comparison to other complexes. The yield can be further raised by collecting a second crop of solid from the filtrate.