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Aldehyde insertion into a platinum hydride and subsequent nucleophilic attack of the alkoxide at phosphorus: platinum-alkoxide/phosphorus-aryl metathesis

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duction to Co(I) was observed, always affording the $[Co(CNR)_3P_2]^+$ derivative.

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Registry No. 1a, 127518-91-6; **1b**, 127518-95-0; **1c**, 127518-97-2; **2a**, 127518-93-8; **2b**, 127518-99-4; **2c**, 127519-01-1; $[Co(CNR)_2P_3]PF_6$ (R = $4\text{-}CH_3C_6H_4$), 127518-87-0; $[Co(CNR)_3P_2]PF_6$ (R = $4\text{-}CH_3C_6H_4$), 127518-89-2; $(4\text{-}CH_3C_6H_4N_2)^+BF_4^-$, 459-44-9.

Aldehyde Insertion into a Platinum Hydride and Subsequent Nucleophilic Attack of the Alkoxide at Phosphorus: Platinum–Alkoxide/Phosphorus–Aryl Metathesis

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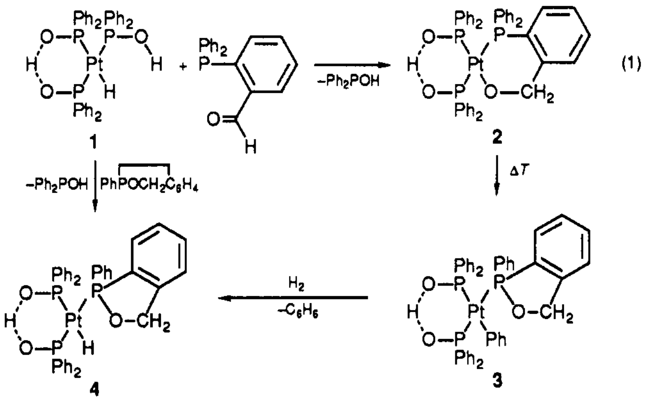
Summary: $Pt(Ph_2PO)(Ph_2POH)_2H$ (**1**) was treated with *o*-(diphenylphosphino)benzaldehyde to give a cyclic platinum alkoxide (**2**). The latter rearranges to the new product **3** (Scheme I), containing 1-phenyl-3*H*-2,1-benzoxaphosphole and a phenyl group coordinated to platinum, via a nucleophilic attack at the coordinated phosphorus center by the alkoxy group, followed by a shift of a phenyl group from phosphorus to platinum. The crystal structure of **3** has been determined.

The insertion of aldehydes into transition-metal hydrides plays a role in industrial processes such as the reduction of aldehydes to alcohols and the conversion of syngas to methanol or ethylene glycol.[1] In recent years the proposed intermediate alkoxide and hydroxymethyl late-transition-metal complexes have been prepared and their reactivity has been studied.[2-9] We have recently reported[10] on platinum phosphinito complexes that catalyze the hydroformylation of alkenes. The aldehydes are hydrogenated to alcohols in a secondary reaction, which may involve either alkoxy or hydroxymethyl intermediates. This communication deals with the mechanism of the aldehyde hydrogenation reaction in a model compound using *o*-(diphenylphosphino)benzaldehyde as the substrate. The resulting complex shows an unexpected rearrangement reaction that is related to the decomposition of arylphosphines in syngas reactions with late-transition-metal catalysts.

Scheme I



When $Pt(Ph_2PO)(Ph_2POH)_2H$ (1) was treated with *o*-(diphenylphosphino)benzaldehyde,[11,12a,b] one of the Ph_2POH ligands was immediately replaced and the resulting product showed that insertion[12c] of the aldehyde into the platinum–hydride bond had occurred. ^1H and ^{31}P NMR spectroscopy revealed[13] that the platinum alkoxide 2 had been formed. Insertion of $Ph_2P(o\text{-}C_6H_4CHO)$ into a metal hydride may give either an alkoxy- or an (α-hydroxyalkyl)metal complex. Thermodynamic studies[2,4,6] indicate that noncyclic alkyl- and alkoxyplatinum species have equal stabilities. In the present reaction both the five-membered ring (with an α-hydroxyalkyl group) and the six-membered ring (with an alkoxy group) should be accessible since chelating phosphinoalkenes[14] react with platinum hydride 1 to give products with ring sizes ranging from three to seven. Molecular models show that the five-membered ring may be slightly more favorable. Also,

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(1) Sisak, A.; Sámpár-Szerencsés, E.; Galamb, V.; Németh, L.; Ungváry, F.; Pályi, G. *Organometallics* **1989**, *8*, 1096 and references therein.

(2) Bryndza, H. E.; Calabrese, J. C.; Marsi, M.; Roe, D. C.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 4805.

(3) Bernard, K. A.; Atwood, J. D. *Organometallics* **1989**, *8*, 795.

(4) Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163.

(5) Park, S.; Pontier-Johnson, M.; Roundhill, D. M. *J. Am. Chem. Soc.* **1989**, *111*, 3101.

(6) Bryndza, H. E.; Fong, L. K.; Paciello, R. A.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 1444.

(7) Hoffman, D. M.; Lappas, D.; Wierda, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 1531.

(8) Kim, Y.-J.; Osakada, K.; Sugita, K.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1988**, *7*, 2182.

(9) Arnold, D. P.; Bennett, M. A. *Inorg. Chem.* **1984**, *23*, 2110.

(10) van Leeuwen, P. W. N. M.; Roobeek, C. F.; Wife, R. L.; Frijns, J. H. G. *J. Chem. Soc., Chem. Commun.* **1986**, 31.

(11) Schiemenz, G. P.; Kaack, H. *Justus Liebigs Ann. Chem.* **1973**, *9*, 1480.

(12) $o\text{-}Ph_2PC_6H_4CHO$ has been employed in reactions with Vaska's complex[12a] and $PtCl_2$[12b] to give oxidative addition of the aldehyde to the metal: (a) Landvatter, E. F.; Rauchfuss, T. B. *Organometallics* **1982**, *1*, 506. (b) Rauchfuss, T. B. *J. Am. Chem. Soc.* **1979**, *101*, 1045. Depending on the other ligands, the reactions involving aldehyde C–H bond breaking can be very facile, as is the case for quinoline-8-carbaldehyde,[12c] and for the present reaction more complicated mechanisms other than straightforward aldehyde insertion might be envisaged: (c) Anklin, C. G.; Pregosin, P. S. *J. Organomet. Chem.* **1983**, *243*, 101.

(13) ^{31}P NMR for **2** (CD_2Cl_2): $\delta(Ph_2PO)$ 72.0, $^1J(PtP) = 3100$ Hz, $^2J(PP\ trans) = 420$ Hz, $^2J(PP\ cis) = 30$ Hz; $\delta(Ph_2PC_6H_4CH_2O\text{–})$ 13.0, $^1J(PtP) = 2180$ Hz, $^2J(PP\ trans) = 420$ Hz, $^2J(PP\ cis) = 9.0$ Hz; $\delta(Ph_2POH)$ 61.0, $^1J(PtP) = 3420$ Hz, dd, cis couplings. ^1H NMR: δ 3.92 (2 H), $^3J(PH) = 9$ Hz, $^2J(PtH) = 33$ Hz; δ 6.4–8.0 (34 H).

(14) van Leeuwen, P. W. N. M.; Roobeek, C. F.; Frijns, J. H. G.; Orpen, A. G. *Organometallics* **1990**, *9*, 1211.

the benzylic carbon will add to the stability of the α-hydroxymethyl isomer. The observed formation of the alkoxy species with the six-membered ring in reaction 1 (Scheme I) is therefore presumably kinetically controlled. In (DPPE)PtEt(OMe)[2] the reverse reaction, β-hydride elimination, proceeds marginally faster for the ethyl ligand than for the methoxy ligand, but other factors may play a role as well. Calculations indicate[15] that during the insertion of alkenes into a platinum–hydrogen bond the hydrogen develops a more hydridic character and the alkene develops a negative charge in the α-position. Considering an aldehyde as a heteroalkene, we can rationalize the kinetic preference for the alkoxy formation. It has been found[16] that in a similar reaction Mn(CO)$_5$H and Ph$_2$P-(*o*-C$_6$H$_4$CHO) afford an α-hydroxycarbyl complex: metal hydrides that are strongly acidic or are good H-radical donors are regarded[16] to be most suited to follow this pathway under kinetic control (e.g. Co,[1] Mn,[16] Rh[17]).

Several platinum alkoxides have been prepared[2,4] via metathesis reactions, but they have never been obtained via aldehyde insertions; they are reactive species and are labile with respect to β-hydrogen elimination.[18] In complex **2** the alkoxide is entropically stabilized by the chelating phosphine.

In an attempt to form the potentially thermodynamically more stable α-hydroxyalkyl isomer, we heated complex **2** in toluene. Instead of the expected 30–40 ppm downfield shift for the ^{31}P resonance of the chelating (α-hydroxyalkyl)phosphine, characteristic of a five-membered ring,[19] a new resonance was observed at 125.9 ppm. The ^1J(PtP) coupling constant of the phosphinito ligand trans to the former oxygen ligand shifts from 3420 Hz (oxygen trans influence) to the new value of 2061 Hz, in the range typical of a phosphinito ligand trans to a carbon ligand (1900–2300 Hz[14]). The NMR data are consistent[20] with the new complex **3** containing a cyclic phosphinite (or oxaphosphole) ligand. Reaction of **3** with H_2 (90 °C, 20 bar) gave the expected platinum hydride **4** containing 1-phenyl-3*H*-2,1-benzoxaphosphole as the ligand and 1 mol of benzene. The structure of the latter hydride **4** was proven by an independent synthesis.[21] The structure of **3** was confirmed by an X-ray crystallographic analysis.[22] The molecule consists of a platinum atom that is indeed σ-bonded to a phenyl group, a chelated diphenylphosphinous acid/diphenylphosphinito ligand, and the cyclic phosphinite ligand 1-phenyl-3*H*-2,1-benzoxaphosphole (see Figure 1). The coordination geometry is nominally square planar as would be expected for Pt(II), but there are some significant deviations from ideal angle values, especially where the oxaphosphole ligand is involved.[22] Furthermore, the coordination plane is puckered with the PtP(1)C(1) and PtP(2)P(3) planes misaligned by a dihedral angle of 13.6°. These distortions are probably due to steric crowding, although, in addition, the strained oxaphosphole ring may require near-coplanarity with the coordination plane so as to maximize π-back-donation into the P σ* orbitals. The intra-ring angle O(1)–P(1)–C(13) is well below typical acyclic values (ca. 102–104°) at 94.2 (4)°.

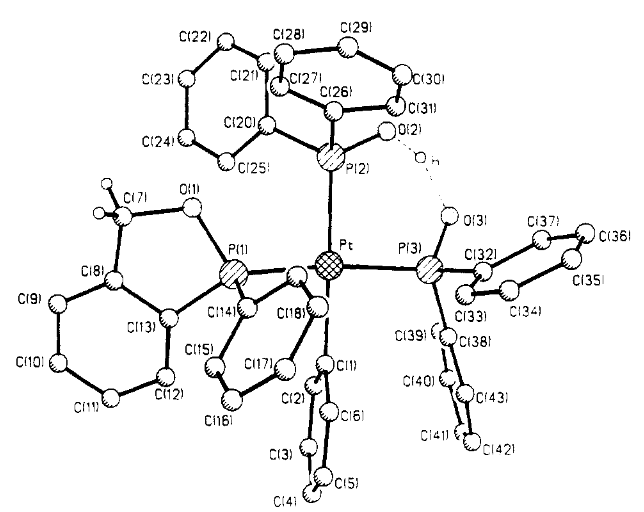

Figure 1. Structure of **3** viewed almost perpendicular to the coordination plane of platinum. Phosphorus-bound phenyl groups are represented by their ipso carbons only, for clarity. All aryl hydrogens are omitted.

The rearrangement of **2** to **3** is best described as a nucleophilic attack of the alkoxy group at the coordinated phosphorus center followed by a shift of a phenyl group from phosphorus to platinum. In this case a relatively stable oxaphosphole is formed. Attack of a nonchelating alkoxide would give a less stable acyclic phosphinite ester that could easily undergo further reaction to phosphido species under the forcing conditions applied for catalytic hydroformylation or hydrogenation. Nucleophilic displacement plays a crucial role in the decomposition of arylphosphines in late-transition-metal catalysis. For example, it has been proposed that acetate ions attack palladium-coordinated triphenylphosphine with concurrent migration of the phenyl group to palladium to give diphenylphosphido complexes and benzene derivatives.[23,24]

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(15) Koga, N.; Obara, S.; Kitaura, K.; Morokuma, K. *J. Am. Chem. Soc.* **1985**, *107*, 7109.

(16) Vaughn, G. D.; Strouse, C. E.; Gladysz, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 1462.

(17) van Voorhees, S. L.; Wayland, B. B. *Organometallics* **1985**, *4*, 1887.

(18) Bennett, M. A.; Yoshida, T. *J. Am. Chem. Soc.* **1978**, *100*, 1750.

(19) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

(20) ^{31}P NMR for **3** (CD$_2$Cl$_2$, data in parentheses in C$_7$D$_8$): δ(Ph$_2$PO) 75.8 (76.9), ^1J(PtP) = 2910 Hz, ^2J(PP trans) = 479 (476) Hz, ^2J(PP cis) = 29.2 Hz; δ(PhPOCH$_2$C$_6$H$_4$) 125.9 (130.3), ^1J(PtP) = 2730 (2685) Hz, ^2J(PP trans) = 479 (476) Hz, ^2J(PP cis) = 23.0 Hz; δ(Ph$_2$POH) 86.1 (87.1), ^1J(PtP) = 2061 Hz, dd, cis couplings. ^{1}H NMR (CD$_2$Cl$_2$): δ 4.52 dd (1 H), ^2J(HH) = 13.5 Hz, ^3J(PH) = 12 Hz; δ 5.03 dd (1 H), ^2J(HH) = 13.5 Hz, ^3J(PH) = 2.2 Hz, ^3J(HPt) = 17 Hz; δ 5.83 t (1 H) (C$_6$H$_4$); δ 6.4–8.0 (33 H); δ 17.4 (1 H), O–H–O. Anal. Calcd for **3**·C$_7$H$_8$ (C$_{50}$H$_{45}$O$_3$P$_3$Pt): C, 61.19; H, 4.62; P, 9.41; Pt, 19.88. Found: C, 61.20; H, 4.56; P, 9.28; Pt, 19.78.

(21) 1-Phenyl-3*H*-2,1-benzoxaphosphole (^{31}P NMR δ 121.3, in CD$_2$Cl$_2$) was prepared in moderate yield as reported: Dahl, B. M.; Dahl, O.; Trippett, S. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2239. **4** was synthesized from equimolar amounts of **1** and 1-phenyl-3*H*-2,1-benzoxaphosphole in 60% yield. ^{31}P NMR (CD$_2$Cl$_2$): δ(Ph$_2$PO) 81.4, ^1J(PtP) = 2752 Hz, ^2J(PP trans) = 443 Hz, ^2J(PP cis) = 29.8 Hz; δ(PhPOCH$_2$C$_6$H$_4$) 140.1, ^1J(PtP) = 2637 Hz, ^2J(PP trans) = 443 Hz, ^2J(PP cis) = 23.4 Hz; δ(Ph$_2$POH) 90.7, ^1J(PtP) = 2318 Hz, dd, cis couplings. ^{1}H NMR (CD$_2$Cl$_2$): δ 4.65 dd (1 H), ^2J(HH) = 13 Hz, ^3J(PH) = 11 Hz; δ 5.39 dd (1 H), ^2J(HH) = 13 Hz, ^3J(PH) = 2 Hz, ^3J(HPt) = 18 Hz; δ −3.40 ddd (1 H) (hydride), ^1J(HPt) = 880 Hz, ^2J(HP$_{trans}$) = 149 Hz, ^2J(HP$_{cis}$) = 12 and 30 Hz; δ 6.6–8.0 (29 H).

(22) Crystal data for **3**·C$_7$H$_8$ (C$_{50}$H$_{45}$O$_3$P$_3$Pt): M_r = 981.92; space group $P2_1/c$ (No. 14); a = 20.243 (5) Å, b = 12.884 (3) Å, c = 16.697 (4) Å; β = 94.06 (2)°; V = 4344 (2) Å^3; Z = 4; d_{calc} = 1.50 g cm^{-3}; Nicolet R3m instrument; room temperature; μ(Mo Kα) = 34.1 cm^{-1}; scan method ω(Wyckoff); data collection range $4 < 2\vartheta < 50°$; number of unique data 7698; number of total data used 5625 ($I > 2\sigma(I)$); solution by heavy-atom methods (Patterson and Fourier) with full-matrix least-squares refinement to convergence (refined parameters 516); R = 0.052, R_w = 0.057, S = 1.55; final residual 0.95 e Å^{-3}, near solvate and heavy atoms. Salient bond lengths (Å): Pt–P(1) = 2.274 (2); Pt–P(2) = 2.307 (2); Pt–P(3) = 2.307 (2); Pt–C(1) = 2.097 (9); P(1)–O(1) = 1.618 (6). Bond angles (deg): P(1)–Pt–P(2) = 97.0 (1); P(1)–Pt–P(3) = 166.7 (1); P(3)–Pt–P(2) = 90.2 (1); P(1)–Pt–C(1) = 85.0 (2); P(2)–Pt–C(1) = 173.0 (3); P(3)–Pt–C(1) = 89.1 (2); Pt–P(1)–O(1) = 117.6 (2); O(1)–P(1)–C(13) = 94.2 (4); O(1)–P(1)–C(14) = 104.8 (4); Pt–P(1)–C(13) = 125.1 (3); Pt–P(1)–C(14) = 106.7 (3).

Transfer of an aryl group from triphenylphosphine to a diruthenium species has been reported to take place along with a synergic joining of an oxygen atom from a bridging amide to the phosphorus atom.[25] Also, in the fast rhodium-catalyzed decomposition of triphenylphosphine in the presence of formaldehyde[26] we propose that the first step involves attack of the methoxy ligands at the coordinated phosphine. The rearrangement of **2** to **3** is the first well-defined case of an alkoxy ligand assisted phosphorus–carbon bond cleavage in a triarylphosphine. It shows that ortho metalation or cluster-assisted reactions are not necessarily involved in P–C bond cleavage. The present P–C/Pt–O metathesis may have been somewhat overlooked as a phosphine decomposition mode of homogeneous catalysts:[27,28] it may be especially important in syngas reactions where metal alkoxides are likely intermediates.

Registry No. **1**, 126135-74-8; **2**, 127973-52-8; **3**, 127973-53-9; **3**·C_7H_8, 127973-55-1; **4**, 127973-54-0; *o*-(diphenylphosphino)benzaldehyde, 50777-76-9; 1-phenyl-3*H*-2,1-benzoxaphosphole, 79157-82-7.

Supplementary Material Available: Details of the structure determination and listings of crystal data, positional and thermal parameters, and bond distances and angles for **3** (7 pages); a listing of observed and calculated structure factors for **3** (28 pages). Ordering information is given on any current masthead page.

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(23) Kikukawa, K.; Takagi, M.; Matsuda, T. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1493.

(24) Sisak, A.; Ungvâry, F.; Kiss, G. *J. Mol. Catal.* **1983**, *18*, 223.

(25) Chakravarty, A. R.; Cotton, F. A. *Inorg. Chem.* **1985**, *24*, 3584.

(26) Kaneda, K.; Sano, K.; Teranishi, S. *Chem. Lett.* **1979**, 821. In a typical reaction 0.05 mmol of $Rh_6(CO)_{16}$, 1 mmol of PPh_3, and 2.5 mmol of paraformaldehyde were heated at 80 °C under 6–8 bar of CO in dioxane (1% H_2O) for 24 h. Analysis showed that 1 mmol of benzaldehyde was formed. Phosphorus NMR spectra showed a variety of phenyl- and diphenylphosphorus oxide complexes or, more precisely, their formaldehyde adducts.

(27) A reviewer pointed out that there still is the possibility that a classical P–C(phenyl) bond splitting occurs, preceded by Pt–alkoxide dissociation, followed by attack of the alkoxide at the phosphido intermediate. Prolonged hydroformylation experiments did not show any P–C bond breaking of tris(*p*-tolyl)phosphine.[14]

(28) For a review on transition-metal-mediated phosphorus–carbon bond cleavage and its relevance to homogeneous catalysis see: (a) Garrou, P. E. *Chem. Rev.* **1985**, *85*, 171. Other examples of nucleophilic attack at coordinated phosphorus by oxo ligands have been reported: (b) Al-Jibori, S.; Hall, M.; Hutton, A. T.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1982**, 1069. (c) Beck, W.; Keubler, M.; Leidl, E.; Nagel, U.; Schaal, M.; Cenini, S.; Del Buttero, P.; Licandro, E.; Maiorana, S.; Chiesi Villa, A. *J. Chem. Soc., Chem. Commun.* **1981**, 446. (d) Bouaoud, S.-E.; Braunstein, P.; Grandjean, D.; Matt, D. *Inorg. Chem.* **1986**, *25*, 3765. (e) Alcock, N. W.; Bergamini, P.; Kemp, T. J.; Pringle, P. G. *J. Chem. Soc., Chem. Commun.* **1987**, 235.

Synthesis of Isomeric Complexes (μ-H)$W_2(CO)_7(RNC)_2(NO)$ (R = Me, ^{t}Bu, $PhCH_2$): X-ray Structures of (μ-H)$W_2(CO)_7(THF)_2(NO)$ and Isomeric (μ-H)$W_2(CO)_7(MeNC)_2(NO)$ with Bent Staggered/Eclipsed Conformations

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Summary: Reactions of (μ-H)$W_2(CO)_9(NO)$ and (μ-H)$W_2(CO)_7(THF)_2(NO)$ with excess RNC (R = Me, ^{t}Bu, $PhCH_2$) afford the yellow complexes (μ-H)$W_2(CO)_7(RNC)_2(NO)$ and reddish isomers, respectively; X-ray structural studies on (μ-H)$W_2(CO)_7(THF)_2(NO)$ and an isomeric pair of (μ-H)$W_2(CO)_7(MeNC)_2(NO)$ complexes are described. The reddish isomers of the type (μ-H)$W_2(CO)_7(MeNC)_2(NO)$ exhibit bent, eclipsed conformations.

Transition-metal complexes with bridging hydride ligands have attracted considerable interest in the past.[1] It is believed that a linear M–H–M geometry is inherently less stable than a bent geometry since the latter permits a smaller M–M distance with a stronger 3c–2e bonding interaction.[2] A recent report suggested that the M–H–M bond can in fact be described as flexible in the case of carbonyl dimers with single hydrogen bridges.[3] To date only two complexes, $HCr_2(CO)_{10}^-$ and $HW_2(CO)_{10}^-$, have been found to have both carbonyl-staggered and carbonyl-eclipsed geometries,[2,4] however. We now report that both staggered and eclipsed conformations also exist in the isocyanide derivatives of $HW_2(CO)_9(NO)$,[5] $HW_2(CO)_7(RNC)_2(NO)$. Earlier we[6] characterized several phosphine-substituted derivatives of $HW_2(CO)_9(NO)$, all of which possess a bent W–H–W linkage with the equatorial groups staggered and the nitrosyl ligand occupying the axial position on the phosphine-substituted tungsten, similar to the case for $HW_2(CO)_8(P(OMe)_3)(NO)$.[7]

Reaction of $HW_2(CO)_9(NO)$ with excess RNC (R = Me, ^{t}Bu, $PhCH_2$) in CH_2Cl_2 at 25 °C for 3 h affords, after subsequent workup, the yellow complexes (μ-H)$W_2(CO)_7(RNC)_2(NO)$ in 33, 36, and 6% yields for R = ^{t}Bu

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(1) E.g.: (a) Dahl, L. F. In *Catalytic Transition Metal Hydrides*; New York Academy of Science: New York, 1983; Part I. (b) Venanzi, L. M. *Coord. Chem. Rev.* **1982**, *43*, 251 and references cited therein.

(2) (a) Bau, R.; Koetzle, T. F. *Pure Appl. Chem.* **1978**, *50*, 55. (b) Bau, R.; Teller, R. G.; Koetzle, T. F. *Acc. Chem. Res* **1979**, *12*, 176.

(3) Jezowska-Trzebiatowska, B.; Nissen-sobocinska, B. *J. Organomet. Chem.* **1987**, *322*, 331.

(4) (a) Petersen, J. L.; Brown, R. K.; Williams, J. M.; McMullan, R. K. *Inorg. Chem.* **1979**, *18*, 3493. (b) Roziere, J.; Williams, J. M.; Stewart, R. P., Jr.; Petersen, J. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1977**, *99*, 4497. (c) Wilson, R. D.; Graham, S. A.; Bau, R. *J. Organomet. Chem.* **1975**, *91*, C49. (d) Handy, L. B.; Ruff, J. K.; Dahl, L. F. *J. Am. Chem. Soc.* **1970**, *92*, 7312. (e) Handy, L. B.; Treichel, P. M.; Dahl, L. F.; Hayter, R. G. *J. Am. Chem. Soc.* **1966**, *88*, 366.

(5) Olsen, J. P.; Koetzle, T. F.; Kirtley, S. W.; Andrews, M.; Tipton, D. L.; Bau, R. *J. Am. Chem. Soc.* **1974**, *96*, 6621.

(6) Lin, J. T.; Wang, S. Y.; Huang, P. S.; Hsiao, Y. M.; Wen, Y. S.; Yeh, S. K. *J. Organomet. Chem.*, in press.

(7) Love, R. A.; Chin, H. B.; Koetzle, T. F.; Kirtley, S. W.; Whittlesty, B. R.; Bau, R. *J. Am. Chem. Soc.* **1976**, *98*, 4491.