

- (14) (a) S. Manastyrskij and M. Dubeck, *Inorg. Chem.*, **3**, 1697 (1964); (b) F. Calderazzo, R. Pappalardo, and S. Losi, *J. Inorg. Nucl. Chem.*, **28**, 987 (1966); (c) E. O. Fischer and H. Fischer, *J. Organomet. Chem.*, **6**, 141 (1966).
- (15) Attempts to isolate a burgundy samarium complex have been unsuccessful. Precipitation with hexane or removal of THF causes the resulting solid to revert to a yellow color.
- (16) Color changes in THF solutions have also been observed for some other Cp_2LnR complexes, but no general trends with regard to ligands can be discerned.
- (17) It is, of course, possible that this band in the Er spectrum is a new band, and coincidentally absorbs at the same place as the weak band already present.
- (18) Work done in partial requirement for the Ph.D. degree at TAMU.

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Hydridotrichlorostannatocarbonylbis(triphenylphosphine)platinum(II), $PtH(SnCl_3)(CO)(PPh_3)_2$, as a Selective Hydroformylation Catalyst

Sir:

There are relatively few literature references to the use of platinum complexes as hydroformylation catalysts, and these few appear only in the patent literature¹⁻³ and none of them are hydrido complexes. We have prepared the new complex, $PtH(SnCl_3)(CO)(PPh_3)_2$ (**1**) and have found that it is an active catalyst for the hydroformylation of 1-pentene at 100° and 3000 psi of synthesis gas ($CO-H_2 = 1:1$). Analysis of the aldehydes in the product showed more than 95% of the straight chain compound, hexanal. The crystalline catalyst can be recovered unchanged from the reaction mixture and may be reused without any loss of activity.

Other platinum(II) hydrides that are converted to the carbonyl complex under the reaction conditions may be used as catalysts. Thus *trans*- $[PtH(SnCl_3)(PPh_3)_2]$ (**2**) or *trans*- $[PtHCl(PPh_3)_2]$ (**3**), to which excess $SnCl_2 \cdot 2H_2O$ (mole ratio 1:5) is added, also function as effective catalysts, and **1** can be recovered from the reaction mixtures.

The reported method⁴ for the preparation of **2** was modified. To a stirred solution of *trans*- $[PtHCl(PPh_3)_2]$ ⁵ (0.76 g), benzene (25 ml), and ether (75 ml) was added 1.2 g $SnCl_2 \cdot 2H_2O$. After stirring the mixture for 30 min, the orange-yellow precipitate of **2** was filtered and washed with ether, yield 0.76 g.

A suspension of 5 g of **2** in 250 ml of benzene was placed in a 300-ml autoclave. After the autoclave was flushed three times with N_2 (1000 psi) and once with CO (1000 psi), the autoclave was charged with CO (1500 psi) and with H_2 (1500 psi), and the mixture was heated at 100°. After 6 hr, the autoclave was cooled and depressured, whereupon greenish yellow crystals separated from the solution. These crystals were filtered and washed with benzene and then with pentane: yield 4.1 g; mp 93-95° dec; $\nu_{(Pt-H)}$ 2165 cm^{-1} , $\nu_{(C=O)}$ 2050 cm^{-1} , $\nu_{(Sn-Cl)}$ 335, 314, 292 cm^{-1} (Nujol mull). Anal. Calcd: C, 45.6; H, 3.2; Cl, 10.9. Found: C, 45.4; H, 3.2; Cl, 10.5.

At the present time, we are unsure of the exact structure of the relatively unstable complex, **1**. It may be a four-coordinate ionic salt, $[Pt(H)(CO)(PPh_3)_2]^+SnCl_3^-$, analogous to the corresponding known⁶ BPh_4^- salt, or it may be a five-coordinate compound, in which case it would be quite unusual. On drying under vacuum, or on exposure to air for several days, it loses CO and gives *trans*- $[PtH(SnCl_3)(PPh_3)_2]$. Attempts to recrystallize the carbonyl complex resulted in the formation of *trans*- $[PtHCl(PPh_3)_2]$ with extrusion of CO and $SnCl_2$.

A typical hydroformylation reaction was performed as follows. $PtH(SnCl_3)(CO)(PPh_3)_2$ (2.4 g, 2.5 mmol) and 150 ml of benzene were charged into a 300-ml autoclave which was equipped with an equalizing pressure addition vessel containing 1-pentene (17.5 g, 250 mmol). After the autoclave was sealed and flushed with N_2 and CO , H_2 (1500 psi) and CO (1500 psi) were charged, and the solution was heated to 100° with stirring. 1-Pentene was then added to the autoclave and the reaction mixture stirred with heating for 2.5 hr. The product was analyzed by GLC; essentially all the olefin had disappeared and the aldehyde product consisted of 95% hexanal and 5% 2-methylpentanal.

Essentially similar results were obtained when complexes **2** or **3** (to which was added $SnCl_2 \cdot 2H_2O$) were employed as catalysts.

The rate of the reaction catalyzed by **1** is about five times that of a $Co_2(CO)_8$ -catalyzed reaction carried out under the same conditions. Although a $Co_2(CO)_6(PR_3)$ catalyst⁷ also leads to relatively high selectivity to straight-chain product, the rate of hydroformylation with this catalyst is negligible at 100°. $Rh(Cl)(CO)(PPh_3)_2$ or other modified Rh catalysts operate effectively at 100°, but the ratio of straight- to branched-chain aldehydes⁸ is usually about 3 compared to a ratio of about 20 with the Pt catalyst, **1**.

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References and Notes

- (1) G. Wilkinson, French patent 1,459,643 (1966).
- (2) L. Slaugh and R. D. Mullineaux, U.S. patent 3,239,571 (1966).
- (3) I. Schwager and J. F. Knifton, German patent 2,322,751 (1973).
- (4) M. C. Baird, *J. Inorg. Nucl. Chem.*, **29**, 367 (1967).
- (5) J. C. Bailar, Jr., and H. Iatani, *Inorg. Chem.*, **4**, 1618 (1965).
- (6) H. C. Clark and K. R. Dixon, *J. Am. Chem. Soc.*, **91**, 569 (1969).
- (7) E. R. Tucci, *Ind. Eng. Chem., Prod. Res. Dev.*, **7**, 125 (1968).
- (8) J. H. Craddock, A. Hershman, F. E. Paulik, and J. F. Roth, *Ind. Eng. Chem., Prod. Res. Dev.*, **8**, 291 (1969).

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Characterization of Oligomers of Tetrakis(phenyl isocyanide)rhodium(I) in Acetonitrile Solution

Sir:

There has been considerable recent interest in the optical spectra and electrical conductivities of platinum compounds in which direct metal-metal interactions are present.¹⁻⁶ Perhaps the best known examples are the double salts, such as $[Pt(NH_3)_4][PtCl_4]$ (Magnus' green salt or MGS).¹ Low solubility of the double salts has generally restricted study to solid samples, although it should be noted that Isci and Mason have obtained electronic spectra for certain $[Pt(CNR)_4][Pt(CN)_4]$ complexes in ethanol solution.⁶

Many simple platinum salts also possess unusual properties.^{2,3} The planar ions in these compounds, as in MGS, stack face-to-face in infinite columns. However, with the exception of one or two mixed-valence aggregates, notably $[Pt(C_2O_4)_2]_n^{1.6n-}$, complete dissociation to monomeric fragments occurs in solution. Even the copper-colored, mixed-valence Krogmann's salt, $K_2Pt(CN)_4Cl_{0.3} \cdot 3H_2O$,