*Inorg. Chem.* **1988**, *27*, 3233–3235

67-1; *neo*-$C_5H_{11}Cl$, 753-89-9; $[(n\text{-}Bu)_3PCuI]_4$, 59245-99-7; $CF_3CH_2OH$, 75-89-8; $CF_3CH_2ONa$, 420-87-1.

**Supplementary Material Available:** C–H bond lengths (Tables XI and XII), H–C–X bond angles (Tables XIII and XIV), positional parameters for hydrogen atoms (Tables XV and XVI), selected least-squares planes and distances of atoms from those planes (Tables XVII and XVIII), and thermal parameters (Tables XIX and XX) (10 pages); observed and calculated structure factor amplitudes (Tables XXI and XXII) (60 pages). Ordering information is given on any current masthead page.

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# Notes

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## Platinum(0) Complexes as Catalysts of Metal Carbonyl Substitution Reactions

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Phosphine-substituted metal carbonyls have often been prepared by methods involving thermal or photochemical replacement of a CO ligand, despite several commonly observed problems: low yields, mixtures of mono- to multi-substituted products, and long reaction times.[1] More recently, several new procedures[2] have been developed to promote CO substitution by other ligands under mild conditions. Among them is $Me_3NO$,[3] which oxidatively decarbonylates metal carbonyls, leading to a coordinatively unsaturated intermediate. Sodium benzophenone ketyl (BPK)[4,5] has been shown to catalyze CO substitution. Also, several transition-metal complexes induce catalytic CO displacement in metal carbonyls. These include $[CpFe(CO)_2]_2$,[6] $[CpMo(CO)_3]_2$,[7] $CoCl_2$,[8] PdO,[9] and $Fe_2(CO)_6(SMe)_2$.[10] In most of these reactions, there is evidence for electron-transfer catalysis (ETC) or it has been suggested that ETC is involved. We report here that the Pt(0) complexes $Pt(PPh_3)_4$ and Pt(dibenzylideneacetone)$_2$ (Pt(dba)$_2$) also catalyze the phosphine substitution of CO in mono-, di-, and trinuclear metal carbonyl complexes. These two catalysts offer a convenient, high-yield route to monosubstituted $M_x(CO)_{y-1}L$ complexes where L is a monodentate phosphine ligand.

## Experimental Section

**General Reagents and Procedures.** All reactions were performed under prepurified $N_2$. Unless noted otherwise, reagent grade chemicals were used without further purification. Methylene chloride and hexanes were distilled from $CaH_2$ and stored under $N_2$ over type 4A molecular sieves. Benzene was distilled from sodium benzophenone under $N_2$.

The starting compounds, $W(CO)_6$, $Fe(CO)_5$, $CpMn(CO)_3$, $Re_2(CO)_{10}$, and $Ph_2PCH_2CH_2PPh_2$ (dppe) were purchased from Pressure Chemical Co. Other starting compounds, $CpFe(CO)_2I$,[11] $Re(CO)_5(CH_3)$,[12] $Pt(PPh_3)_4$,[13] and $Pt(dba)_2$,[14] were prepared as reported in the literature. The compound $Os_3(CO)_{12}$ was prepared from $OsO_4$ by a modification of a literature procedure[15] that was carried out in a 300-mL stainless steel pressure autoclave (Parr Model No. 4761).

Infrared spectra were recorded on a Perkin-Elmer 681 instrument. $^1H$ NMR spectra were recorded on a Nicolet NT-300 spectrometer. Electron-impact mass spectra were obtained by using a Finnigan 4000 GC-MS.

**Reaction of Metal Carbonyls with $PPh_3$ in the Presence of $Pt(PPh_3)_4$.** A solution of $PPh_3$ (1–2 equiv), the metal carbonyl compound (1 equiv) ($W(CO)_6$, $Fe(CO)_5$, $CpFe(CO)_2I$, $Re(CO)_5(CH_3)$, $CpMn(CO)_3$, $Re_2(CO)_{10}$ or $Os_3(CO)_{12}$), and $Pt(PPh_3)_4$ (0.1 equiv) was brought to reflux in 50 mL of benzene under an $N_2$ atmosphere. The reactions were monitored by changes in the IR spectra (2200–1600 $cm^{-1}$). At the end of the reaction (as established by the disappearance of the starting material), the solution was cooled to room temperature and the solvent removed under vacuum. The residue dissolved in $CH_2Cl_2$ was then passed through a silica-gel column (2.5 × 15 cm) with 1:1 $CH_2Cl_2$/hexanes as the eluant. The $PPh_3$-substituted products were collected. Recrystallization from $CH_2Cl_2$/hexanes gave the isolated products (percent yields in Table I), which were identified by their IR and $^1H$ NMR spectra (Table I). The catalyst, $Pt(PPh_3)_4$, was recovered. Also shown in Table I are results of control reactions where no Pt(0) catalyst was used.

**Reaction of Metal Carbonyls with Ligands in the Presence of $Pt(dba)_2$.** A 50-mL benzene solution containing a donor ligand ($PPh_3$, $PPh_2Me$, dppe, $P(OMe)_3$, or norbornadiene) (usually 1.5 equiv), a metal carbonyl ($Fe(CO)_5$ or $CpFe(CO)_2I$) (1 equiv), and $Pt(dba)_2$ (0.1 equiv) was refluxed in a Schlenk flask. The reaction was monitored by IR spectroscopy (2200–1600 $cm^{-1}$), and heating was continued until the reaction had gone to completion. The solvent was removed under vacuum; the residue dissolved in $CH_2Cl_2$ was chromatographed (2.5 × 15 cm) on silica gel with 1:1 $CH_2Cl_2$/hexanes as the eluent. The products were recrystallized from $CH_2Cl_2$/hexanes.

## Results and Discussion

The substitution of one CO ligand in a variety of metal carbonyl complexes by $PPh_3$ is catalyzed by $Pt(PPh_3)_4$ (eq 1) in refluxing

$$M_x(CO)_y + PPh_3 \xrightarrow[\text{benzene}]{Pt(PPh_3)_4} M_x(CO)_{y-1}(PPh_3) + CO \quad (1)$$

$$M_x(CO)_y = W(CO)_6,\ Fe(CO)_5,\ CpFe(CO)_2I,\ Re(CO)_5(CH_3),\ Re_2(CO)_{10},\ Os_3(CO)_{12}$$

benzene. As summarized in Table I, the products are isolated in 70–98% yields and the $Pt(PPh_3)_4$ catalyst may be recovered nearly quantitatively. Under the conditions of the reactions, but in the absence of the catalyst, there is essentially no reaction. Only the monophosphine-substituted complexes are obtained even when

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[1] (a) Clifford, A. F.; Mukherjee, A. K. *Inorg. Chem.* **1963**, *2*, 151. (b) Cotton, F. A.; Parish, R. V. *J. Chem. Soc.* **1960**, 1440.

[2] Albers, M. O.; Coville, N. J. *Coord. Chem. Rev.* **1984**, *53*, 227.

[3] (a) Shvo, Y.; Hazum, E. *J. Chem. Soc., Chem. Commun.* **1975**, 829. (b) Koelle, U. *J. Organomet. Chem.* **1978**, *155*, 53. (c) Churchill, M. R.; Lashewycz, R. A.; Shapley, J. R.; Richter, S. I. *Inorg. Chem.* **1980**, *19*, 1277. (d) Luh, T.-Y. *Coord. Chem. Rev.* **1984**, *60*, 255.

[4] (a) Bruce, M. I.; Kehoe, D. C; Matisons, J. G.; Nicholson, B. K.; Rieger, P. H.; Williams, M. L. *J. Chem. Soc., Chem. Commun.* **1982**, 442. (b) Bruce, M. I.; Hambley, T. W.; Nicholson, B. K.; Snow, M. R. *J. Organomet. Chem.* **1982**, *235*, 83. (c) Butts, S. B.; Shriver, D. F. *J. Organomet. Chem* **1979**, *169*, 191.

[5] Bruce, M. I. *Coord. Chem. Rev.* **1987**, *76*, 1.

[6] (a) Coville, N. J.; Albers, M. O.; Singleton, E. *J. Chem. Soc., Dalton Trans.* **1983**, 947. (b) Coville, N. J.; Albers, M. O.; Ashworth, T. V.; Singleton, E. *J. Chem. Soc., Chem. Commun.* **1981**, 408. (c) Coville, N. J.; Darling, E. A. *J. Organomet. Chem.* **1984**, *277*, 105. (d) Albers, M. O.; Coville, N. J.; Singleton, E. *J. Organomet. Chem.* **1982**, *232*, 261. (e) Harris, G. W; Albers, M. O.; Boeyens, J. C. A.; Coville, N. J. *Organometallics* **1983**, *2*, 609. (f) Aime, S.; Botta, M.; Gobetto, R.; Osella, D. *Inorg. Chim. Acta* **1986**, *115*, 129.

[7] (a) Coville, N. J. *J. Organomet. Chem.* **1980**, *190*, C84. (b) Coville, N. J. *J. Organomet. Chem.* **1981**, *218*, 337.

[8] (a) Albers, M. O.; Coville, N. J.; Singleton, E. *J. Chem. Soc., Dalton Trans.* **1982**, 1069. (b) *J. Organomet. Chem.* **1980**, *199*, 55. (c) *J. Organomet. Chem.* **1981**, *217*, 385. (d) Albers, M. O.; Coville, N. J.; Ashworth, T. V.; Singleton, E.; Swanepoel, H. E. *J. Chem. Soc., Chem. Commun.* **1980**, 489.

[9] (a) Albers, M. O.; Coville, N. J.; Singleton, E. *J. Chem. Soc., Chem. Commun.* **1982**, 96. (b) Coville, N. J.; Albers, M. O. *Inorg. Chim. Acta* **1982**, *65*, L7. (c) Albers, M. O.; Coville, N. J.; Singleton, E. *J. Organomet. Chem.* **1982**, *234*, C13. (d) Harris, G. W.; Boeyens, J. C. A.; Coville, N. J. *J. Organomet. Chem.* **1983**, *255*, 87.

[10] Aime, S.; Botta, M.; Gobetta, R.; Osella, D. *Organometallics* **1985**, *4*, 1475.

[11] King, R. B. *Organometallic Syntheses*; Academic; New York, London, 1965; Vol. 1, pp 175–6.

[12] Hieber, W.; Braun, G.; Beck, W. *Chem. Ber.* **1960**, *93*, 901.

[13] Ugo, R.; Cariati, F.; La Monica, G. *Inorg. Synth.* **1968**, *11*, 105.

[14] Cherwinski, W. J.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1974**, 1405.

[15] Bradford, C. W.; Nyholm, R. S. *Chem. Commun.* **1967**, 384.

0020-1669/88/1327-3233$01.50/0

**Table I.** Experimental Conditions for the Reactions of Metal Carbonyls with $PR_3$ Ligands in the Presence of $Pt(PPh_3)_4$ or $Pt(dba)_2$ Catalysts

| | | | | | Pt(0)-catalyzed reacn | | uncatalyzed reacn | |
|---|---|---|---|---|---|---|---|---|
| metal carbonyl (mmol) | ligand (L) | catalyst | mole ratio[a] | product | time | % yield | time | results |
| $W(CO)_6$ (2.5) | $PPh_3$ | $Pt(PPh_3)_4$ | 1:1:0.1 | $W(CO)_5(PPh_3)$[c] | 4 days | 92 | 4 days | NR[b] |
| $Fe(CO)_5$ (2.5) | $PPh_3$ | $Pt(PPh_3)_4$ | 1:2:0.1 | $Fe(CO)_4(PPh_3)$[d] | 5 h | 98 | 19 h | *j* |
| | $PPh_3$ | $Pt(dba)_2$ | 1:1.5:0.1 | $Fe(CO)_4(PPh_3)$[d] | 7 h | 81 | | |
| | $PPhMe_2$ | $Pt(dba)_2$ | 1:2:0.1 | $Fe(CO)_4(PPhMe_2)$ | 1.5 h | 79 | 1.5 h | NR |
| | dppe | $Pt(dba)_2$ | 1:1.5:0.1 | | 8 h | NR | | |
| | $P(OMe)_3$ | $Pt(dba)_2$ | 1:2:0.1 | | 17 h | NR | | |
| | NBD | $Pt(dba)_2$ | 1:2:0.1 | | 17 h | NR | | |
| $CpFe(CO)_2I$ (0.50) | $PPh_3$ | $Pt(PPh_3)_4$ | 1:1:0.1 | $CpFe(CO)(PPh_3)I$[e] | 50 min | 87 | 24 h | NR |
| | $PPh_3$ | $Pt(dba)_2$ | 1:1.5:0.1 | $CpFe(CO)(PPh_3)I$[e] | 50 min | 85 | | |
| | $P(OMe)_3$ | $Pt(dba)_2$ | 1:2:0.1 | $CpFe(CO)[P(OMe)_3]I$[e] | 30 min | 91 | 30 min | *l* |
| | dppe | $Pt(dba)_2$ | 1:1.5:0.1 | $CpFe(dppe)I$[f] | 1 h | 84 | 1 h | *k* |
| $Re(CO)_5(CH_3)$ (10.30) | $PPh_3$ | $Pt(PPh_3)_4$ | 1:1:0.1 | $Re(CO)_4(PPh_3)(CH_3)$[g] | 17 h | 86 | 24 h | NR |
| $Re_2(CO)_{10}$ (0.60) | $PPh_3$ | $Pt(PPh_3)_4$ | 1:1:0.1 | $Re_2(CO)_9(PPh_3)$[h] | 2 days | 72 | 2 days | NR |
| $Os_3(CO)_{12}$ (0.20) | $PPh_3$ | $Pt(PPh_3)_4$ | 1:1:0.1 | $Os_3(CO)_{11}(PPh_3)$[i] | 5 min | 98 | 2 h | NR |
| $CpMn(CO)_3$ (2.50) | $PPh_3$ | $Pt(PPh_3)_4$ | 1:1:0.1 | | 3 days | NR | | |

[a] Metal carbonyl:$PR_3$:catalyst. [b] NR = no reaction. [c] Magee, T. A.; Matthews, C. N.; Wang, T. S.; Wotiz, J. H. *J. Am. Chem. Soc.* **1961**, *83*, 3200. [d] Clifford, A. F.; Mukherjee, A. K. *Inorg. Synth.* **1966**, *8*, 185. [e] (1) Brown, D. A.; Lyons, H. J.; Manning, A. R.; Rowley, J. M. *Inorg. Chim. Acta* **1969**, *3*, 346. (2) Brown, D. A.; Lyons, H. J.; Manning, A. R. *Inorg. Chim. Acta* **1970**, *4*, 428. (3) Haines, R. J.; DuPreez, A. L.; Marais, L. L. *J. Organomet. Chem.* **1971**, *28*, 405. [f] Green, M. L. H.; Whitely, R. N. *J. Chem. Soc. A* **1971**, 1943. [g] McKinney, R. J.; Kaesz, H. D. *J. Am. Chem. Soc.* **1975**, *97*, 3066. [h] Dewitt, D. G.; Fawcett, J. P.; Pöe, A. *J. Chem. Soc., Dalton Trans.* **1976**, 528. [i] Bradford, C. W.; van Bronswijk, W.; Clark, R. J. H.; Nyholm, R. S. *J. Chem. Soc. A* **1970**, 2889. [j] Without catalyst, only traces of $Fe(CO)_4L$ and $Fe(CO)_3L_2$ along with $Fe(CO)_5$ are observed. [k] 18% of $CpFe(CO)_2I$ was unreacted. [l] 83% of $CpFe(CO)_2I$ was unreacted.

2 equiv of $PPh_3$ is used in the reactions, as for $Fe(CO)_5$ and $CpFe(CO)_2I$. Of the metal carbonyls studied, only $CpMn(CO)_3$ failed to undergo $Pt(PPh_3)_4$-catalyzed substitution. $CpMn(CO)_3$ is quite inert to thermal substitution in the absence of catalyst,[16] and attempted PdO-catalyzed[9d] substitution was also unsuccessful.

The reaction between $Re_2(CO)_{10}$ and $PPh_3$ in refluxing xylene for 24 h yields $Re_2(CO)_8(PPh_3)_2$ and *mer-trans*-$HRe(CO)_3(PPh_3)_2$ as the main products.[17] The reaction of $Re_2(CO)_{10}$ with $PMe_2Ph$ is reported[18] to yield mixtures of $Re_2(CO)_9(PMe_2Ph)$ and $Re_2(CO)_8(PMe_2Ph)_2$. The $Cp_2Fe_2(CO)_4$-catalyzed[6d] substitution of $Re_2(CO)_{10}$ with $PPh_3$ was also unsuccessful. However, the present method gives $Re_2(CO)_9(PPh_3)$ in 72% isolated yield.

The reaction of $Os_3(CO)_{12}$ with $PMe_3$ causes extensive cluster fragmentation[19] while the Na-BPK method provides poor yields of di- and trisubstituted products.[4a] However, the $Pt(PPh_3)_4$ catalyst affords a high yield (98%) of the monosubstituted product, $Os_3(CO)_{11}(PPh_3)$, in only 5 min. The $Pt(PPh_3)_4$-catalyzed reaction of $Re(CO)_5(CH_3)$ and $PPh_3$ gives only $Re(CO)_4(PPh_3)(CH_3)$. This product had previously[20] been prepared from the reaction of $Re(CO)_4(PPh_3)(Br)$ with MeLi.

While the mechanism of reaction 1 has not been studied, it may involve electron-transfer catalysis (ETC) in which $Pt(PPh_3)_n$ donates an electron to the metal carbonyl to form a labile 19-electron intermediate that rapidly undergoes substitution by the $PPh_3$. Such a mechanism has been proposed for other[21] catalyzed metal carbonyl substitution reactions. There is good evidence that $Pt(PPh_3)_n$ is capable of being such an electron donor in radical mechanisms for oxidative-addition reactions of $Pt(PR_3)_n$ with alkyl halides.[22]

It has been noted that only monosubstitution occurs in reaction 1. This is reasonable in terms of this mechanism, since the monosubstituted $M_x(CO)_{y-1}(PPh_3)$ products are more electron-rich than $M_x(CO)_y$ and would be poorer acceptors of an electron from the Pt(0) catalyst. Likewise, the catalyzed substitutions of all of the complexes should depend on the electron-accepting abilities of the complexes. Those that are likely to be the best acceptors will have the lowest electron density as measured by their high $\nu(CO)$ force constants. Thus, $Pt(PPh_3)_4$ catalyzes CO substitution in the following complexes with relatively high $\nu(CO)$ force constants (given in parentheses): $Fe(CO)_5$ (17.0 and 16.4 mdyn/Å),[23a] $W(CO)_6$ (16.56 mdyn/Å),[23a] $CpFe(CO)_2I$ (16.45 mdyn/Å),[23b] $Re(CO)_5(CH_3)$ (15.97 and 16.87 mdyn/Å),[23a] $Re_2(CO)_{10}$ (15.92 and 16.57 mdyn/Å),[23c] and $Os_3(CO)_{12}$ (16.53 and 16.79 mdyn/Å).[23d] All of the complexes that react according to eq 1 have $\nu(CO)$ force constants greater than 16.4 mdyn/Å, in contrast to the unreactive $CpMn(CO)_3$, whose low $k_{CO}$ value (15.6 mdyn/Å)[24a] indicates that it is relatively electron-rich and would be a poor electron acceptor.

While the ETC mechanism is consistent with the behavior of reaction 1, it is possible that a different mechanism is involved. Stoichiometric reactions[24,25] of $Pt(PR_3)_4$ with certain metal carbonyls, $Fe_2(CO)_9$ and $Ru_3(CO)_{12}$, even at room temperature yield clusters of the types $Fe_2Pt(CO)_9(PR_3)$ and $RuPt_2(CO)_5(PR_3)_3$. Byproducts of these reactions are the phosphine-substituted metal carbonyls $Fe(CO)_4(PR_3)$, $Fe(CO)_3(PR_3)_2$, and $Ru_3(CO)_{12-n}(PR_3)_n$ ($n$ = 1–3). The reaction of $Pt(PPh_2Me)_4$ with $Os_3(CO)_{12}$ gives only the substituted derivatives $Os_3(CO)_{12-n}(PPh_2Me)_n$ ($n$ = 1, 2).[25] The mechanisms of none of these reactions are known, but they suggest the possibility that clusters are intermediates in the catalyzed reactions in eq 1.

Instead of using $Pt(PPh_3)_4$ as the catalyst in reaction 1, it is also possible to use $Pt(dba)_2$, which under the conditions of the reaction with excess $PPh_3$ is converted to $Pt(PPh_3)_2(dba)$.[14] Thus, the reaction of $Fe(CO)_5$, $PPh_3$, and a catalytic amount of $Pt(dba)_2$ in refluxing benzene gives (Table I) an 81% yield of $Fe(CO)_4(PPh_3)$. Similarly, the $Pt(dba)_2$-catalyzed reaction of $CpFe(CO)_2I$ with $PPh_3$ gives $CpFe(CO)(PPh_3)(I)$. The successful use of $Pt(dba)_2$ as a catalyst for the substitution of CO by $PPh_3$ suggests that other monodentate phosphines could be used in analogous

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(16) Caulton, K. G. *Coord. Chem. Rev.* **1981**, *38*, 1.

(17) Cox, D. J.; Davis, R. *J. Organomet. Chem.* **1980**, *186*, 339.

(18) Harris, G. W.; Boeyens, J. C. A.; Coville, N. J. *J. Chem. Soc., Dalton Trans.* **1985**, 2277.

(19) Martin, L. R.; Einstein, F. W. B.; Pomeroy, R. K. *Inorg. Chem.* **1985**, *24*, 2777.

(20) McKinney, R. J.; Kaesz, H. D. *J. Am. Chem. Soc.* **1975**, *97*, 3066.

(21) Geiger, W. E.; Connelly, N. G. *Adv. Organomet. Chem.* **1985**, *24*, 87; **1984**, *23*, 1.

(22) (a) Hall, T. L.; Lappert, M. F.; Lednor, P. W. *J. Chem. Soc., Dalton Trans.* **1980**, 1448. (b) Lappert, M. F.; Lednor, P. W. *Adv. Organomet. Chem.* **1976**, *14*, 345.

(23) (a) Avanzino, S. C.; Bakke, A. A.; Chen, H. W.; Donahue, C. J.; Jolly, W. L.; Lee, T. H.; Ricco, A. J. *Inorg. Chem.* **1980**, *19*, 1931. (b) Gansow, O. A.; Schexnayder, D. A.; Kimura, B. Y. *J. Am. Chem. Soc.* **1972**, *94*, 3406. (c) Flitcroft, N.; Huggins, D. K.; Kaesz, H. D. *Inorg. Chem.* **1964**, *3*, 1123. (d) Battiston, G. A.; Bor, G.; Dietler, U. K.; Kettle, S. F. A.; Rossetti, R.; Sbrignadello, G.; Stanghellini, P. L. *Inorg. Chem.* **1980**, *19*, 1961.

(24) Bruce, M. I.; Shaw, G.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1972**, 1082.

(25) Bruce, M. I.; Shaw, G.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1972**, 1781.

reactions. Indeed, $Pt(dba)_2$ does catalyze the reaction of $Fe(CO)_5$ and $PPhMe_2$ to give $Fe(CO)_4(PPhMe_2)$ and the reaction of $CpFe(CO)_2I$ and $P(OMe)_3$ to give $CpFe(CO)[P(OMe_3](I)$. The reaction of $CpFe(CO)_2I$ and $Ph_2PCH_2CH_2PPh_2$(dppe) to produce CpFe(dppe)I in the presence of $Pt(dba)_2$ is complete within 1 h, and the isolated yield is 84%. Without $Pt(dba)_2$, the reaction is not complete (18% of $CpFe(CO)_2I$ remained unreacted) under the same conditions. There was no observed $Pt(dba)_2$ catalysis of the reactions of $Fe(CO)_5$ with dppe, $P(OMe)_3$, or 2,5-norbornadiene (NBD), which suggests that the method may be limited to monodentate phosphines.

## Conclusion

There are several attractive features of the $Pt(PPh_3)_4$-catalyzed method of substituting a CO ligand in metal carbonyls by $PPh_3$: (a) The reaction cleanly provides monosubstituted products in high yields (70–98%). (b) The catalyst can be recovered almost quantitatively at the end of the experiment. (c) For clusters that tend to fragment under other conditions, the $Pt(PPh_3)_4$ method yields the intact clusters. (d) $k_{CO}$ values are helpful for predicting metal carbonyl complexes to which the method can be applied. The substitution of one CO in $Fe(CO)_5$ and $CpFe(CO)_2I$ by $PPh_3$ and/or $PMe_2Ph$ is also catalyzed by $Pt(dba)_2$, suggesting that $Pt(dba)_2$ may be used more generally to catalyze monodentate phosphine substitution of metal carbonyls.

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**Registry No.** dppe, 1663-45-2; NBD, 121-46-0; $W(CO)_6$, 14040-11-0; $Fe(CO)_5$, 13463-40-6; $CpFe(CO)_2I$, 12078-28-3; $Re(CO)_5CH_3$, 14524-92-6; $Re_2(CO)_{10}$, 14285-68-8; $Os_3(CO)_{12}$, 15696-40-9; $CpMn(CO)_3$, 12079-65-1; $PPh_3$, 603-35-0; $PPhMe_2$, 672-66-2; $P(OMe)_3$, 121-45-9; $Pt(PPh_3)_4$, 14221-02-4; $W(CO)_5(PPh_3)$, 15444-65-2; $Fe(CO)_4(PPh_3)$, 14649-69-5; $Fe(CO)_4(PPhMe_2)$, 37410-37-0; $CpFe(CO)(PPh_3)I$, 12099-18-2; CpFe(dppe)I, 55451-49-5; $CpFe(CO)[P(OMe)_3]I$, 31781-71-2; $Re(CO)_4(PPh_3)(CH_3)$, 56474-50-1; $Re_2(CO)_9(PPh_3)$, 27770-63-4; $Os_3(CO)_{11}(PPh_3)$, 30173-88-4; $Pt(dba)_2$, 33677-56-4.

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# Reappraisal of the Amide Coordination Mode: Solution Properties of Nickel(II) and Copper(II) Complexes of Ligands Involving Simultaneously Enamine and Amide Groups

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Depending on experimental conditions, primary and secondary amide groups are known to bind copper(II) and nickel(II) ions with or without deprotonation.[1] It is generally accepted that, in the former case, coordination occurs through the nitrogen atom while, in the latter case, the carbonyl oxygen is the coordination site. This mode of bonding is largely supported by structural studies,[2,3] but there remains the possibility that the data obtained for solid samples may not be directly applicable to species in solution and that, in some instances, the intact amide nitrogen could serve as the coordinating site. Furthermore, it may be recognized that before considering the problem of the coordinating site (oxygen vs nitrogen), one has to demonstrate unambiguously whether the amide group is intact or not. This is not a trivial problem in the cases where the ligand bonded to the metal ions contains more than one type of ionizable proton.

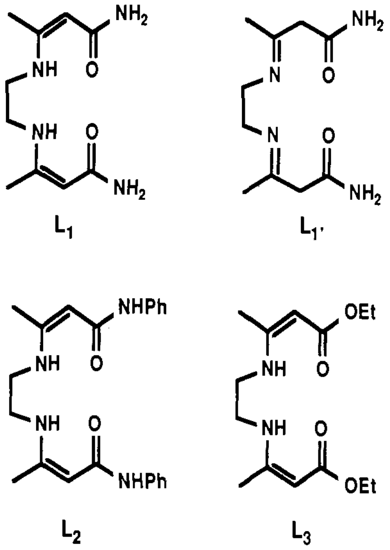

**Figure 1.** $L_1$, $L_2$, and $L_3$ ligands.

This happens for the complex $[CuL_1]^{2+}$ (Figure 1), $L_1$ being the Schiff base resulting from the condensation of 1 mol of 1,2-diaminoethane with 2 mol of acetoacetamide. It has been recently proposed,[4] on the basis of potentiometric, spectrophotometric, and ESR data, that the behavior of aqueous solutions of this complex may be depicted by an equilibrium involving the $[CuL_1]^{2+}$, $[Cu(L_1\text{-}H)]^+$ and $[Cu(L_1\text{-}2H)]$ species ($L_1$-H and $L_1$-2H representing respectively the mono- and dideprotonated forms of $L_1$). The point of importance is that, in the three species, the ligand is considered to be a diimino diamide (form $L_{1'}$ in Figure 1) which contains only one type of ionizable proton, viz., those of the amide groups. However, there is no reason to rule out the possibility for the ligand to be in another tautomeric form that can be described as a dienediamino diamide (form $L_1$ in Figure 1) with two types of ionizable proton.

In the present paper we intend to reappraise the behavior of the $Cu^{2+}/L_1$ system in solution through the isolation and characterization of the copper(II) complexes involving the ligand $L_1$ (or $L_{1'}$) in different states of deprotonation. This study includes the homologous nickel(II) complexes and also the copper(II) and nickel(II) complexes of two related ligands $L_2$ and $L_3$ (Figure 1).

## Experimental Section

**Ligand Preparation.** The $L_1$ ligand, 3,8-dimethyl-4,7-diazadeca-2,8-diene-1,10-diamide, was synthesized from acetoacetamide and 1,2-diaminoethane as previously described.[4]

$L_1$. $^{13}C\{^1H\}$ NMR in DMSO: 15.8 ($CH_3$), 40.7 ($CH_2$), 82.8 (CH), 155.0 (CN), 169.5 ppm (CO).

$L_2$ and $L_3$ ligands were similarly obtained by respectively using acetoacetanilide and ethylacetoacetate instead of acetoacetamide.

$L_2$ **(*N,N'*-Diphenyl-3,8-dimethyl-4,7-diazadeca-2,8-diene-1,10-diamide).** Anal. Calcd for $C_{22}H_{26}N_4O_2$: C, 69.8; H, 6.9; N, 14.8. Found: C, 69.4; H, 7.0; N, 14.7. $^{13}C\{^1H\}$ NMR in $CDCl_3$: 19.4 ($CH_3$), 43.9 ($CH_2$), 85.8 (CH), 139.0 (CN), 119.8 (*o*), 128.8 ppm (*m*), 122.9 (*p*) (phenyl ring), 160.2 (CN), 169.0 ppm (CO).

$L_3$ **(Diethyl 3,8-Dimethyl-4,7-diazadeca-2,8-diene-1,10-dioate).** Anal. Calcd for $C_{14}H_{24}N_2O_4$: C, 59.1; H, 8.5; N, 9.9. Found: C, 58.8; H, 8.6; N, 9.7. $^{13}C\{^1H\}$ NMR in $CDCl_3$: 14.5 ($CH_3CH_2$), 19.1 ($CH_3$), 43.7 ($CH_2$), 58.3 ($CH_3CH_2$), 83.4 (CH), 161.1 (CN), 170.4 ppm (CO).

**Complexes of $L_1$. $L_1Cu(NO_3)_2$.** This compound was prepared as described previously.[4]

**($L_1$-2H)Cu.** $L_1Cu(NO_3)_2$ (0.5 g) was dissolved in 50 mL of ethanol. NaOH (0.1 g) in 1 mL of water then was added dropwise, inducing the precipitation of gray precipitate with a quantitative yield. Anal. Calcd for $C_{10}H_{16}CuN_4O_2$: C, 41.7; H, 5.6; Cu, 22.1; N, 19.5. Found: C, 41.1; H, 5.5; Cu, 21.8; N, 19.5.

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(1) Sigel, H.; Martin, B. *Inorg. Chem.* **1982**, *82*, 385.
(2) Freeman, H. C.; Robinson, G.; Schoene, J. C. *Acta Crystallogr.* **1964**, *17*, 719.
(3) Freeman, H. C.; Schoene, J. C.; Sime, J. G. *Acta Crystallogr.* **1965**, *18*, 381.
(4) Lim, M. C.; McCool, B. J. *Inorg. Chem.* **1984**, *23*, 1192.

0020-1669/88/1327-3235$01.50/0