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# Ambidentate coordination of the tripyridyl ligands 2,2′:6′,2″-terpyridyl, tris(2-pyridyl)-amine, tris(2-pyridyl)methane and tris(2-pyridyl)phosphine to carbonylrhenium centres: structural and spectroscopic studies*

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**The reactions of [Re(CO)$_5$Cl] with the ligands tpy (2,2′:6′,2″-terpyridine), py$_3$N {tris(2-pyridyl)-amine}, py$_3$CH {tris(2-pyridyl)methane}, and py$_3$P {tris(2-pyridyl)phosphine} in toluene solution realize compounds with the general formulation [Re(ligand)(CO)$_3$Cl] in which the tripyridyl ligands are bidentate. X-ray structural determinations of *fac*-[Re(tpy)(CO)$_3$Cl].H$_2$O and *fac*-[Re(py$_3$N)(CO)$_3$Cl] confirm these assignments. [Re(tpy)(CO)$_3$Cl].H$_2$O ($C_{18}H_{13}ClN_3O_4Re$) is monoclinic, space group $P2_1/n$, with cell dimensions $a = 7.432(2)$ Å, $b = 17.016(4)$ Å, $c = 14.466(2)$ Å, $\beta = 93.51(2)°$, and $Z = 4$; full-matrix least-squares refinement on 2435 reflections with $I \geqslant 2.5\sigma(I)$ converged to a final $R = 0.028$ and $R_w = 0.029$. [Re(py$_3$N)(CO)$_3$Cl] ($C_{18}H_{12}ClN_4O_3Re$) is triclinic, space group $P\bar{1}$ with cell dimensions $a = 13.761(2)$ Å, $b = 14.636(6)$ Å, $c = 11.110(2)$ Å, $\alpha = 110.70(2)°$, $\beta = 102.45(2)°$, $\gamma = 107.48(2)°$, and $Z = 4$; full-matrix least-squares refinement on 3459 reflections with $I \geqslant 2.5\sigma(I)$ converged to a final $R = 0.038$ and $R_w = 0.039$. If the synthetic procedure is undertaken under irradiation by visible light, for the ligand py$_3$N a species [Re(py$_3$N)(CO)$_2$Cl] (characterized by infrared spectroscopy and conductance measurements) is also formed, in which the ligand py$_3$N is tridentate. No analogous tridentate species is formed with the ligands tpy or py$_3$P, although there is evidence that it also forms for py$_3$CH.**

**Keywords: Rhenium, carbonyl, terpyridyl, tris(2-pyridyl)amine, tris(2-pyridyl)methane, tris(2-pyridyl)phosphine, structure**

## INTRODUCTION

Interest in the chemistry of the ‘Greenhouse’ gas carbon dioxide has increased substantially in recent years: in particular, its conversions to C$_1$ feedstocks for chemicals manufacture (e.g. carbon monoxide, formaldehyde, methanol) or to potential fuels (e.g. methanol, methane) have attracted particular attention. The direct electrochemical reduction of CO$_2$ at metal electrodes is generally non-specific and is attended by large overpotentials. However, a number of molecular electrocatalysts have been developed which mediate the electrochemical reduction and substantially reduce the overpotential.[1]

One such group of catalysts are the polypyridine complexes of rhenium of the general form [Re(L—L)(CO)$_3$X] {L—L = 2,2′-bipyridine (bpy) or 1,10-phenanthroline (phen), or their derivatives; X = Cl or Br}, which have been studied particularly by Hawecker *et al.*,[3] Meyer and Sullivan and co-workers,[3-5] and Kutal *et al.*[6] The complexes act as efficient homogeneous catalysts for the selective and sustained reduction of CO$_2$ to carbon monoxide (CO); furthermore, the reduction can be promoted either electrochemically or photochemically. The large turnover numbers observed are a consequence in part of

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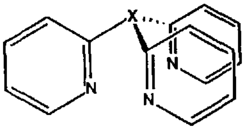
* Supplementary material is lodged with the Cambridge Crystallographic Data Centre, UK.

the stability of the catalyst with respect to deactivation reactions with the dominant product, CO. Despite the considerable attention directed towards the reactivity of $CO_2$ with such catalysts, the intimate mechanism of the reduction of $CO_2$ is a matter of considerable conjecture.[4] The elucidation of the key electron-, proton- and atom-transfer steps in such processes is clearly required for the rational design of effective catalysts.

With this in mind, we undertook a study of the synthesis and reactivities of a series of carbonylrhenium compounds incorporating the ligands $py_3X$, where $py_3X$ represents the ligands tris(2-pyridyl)amine ($py_3N$), tris(2-pyridyl)methane ($py_3CH$), and tris(2-pyridyl)phosphine ($py_3P$). These tripodal $\pi$-acceptor ligands offer a greater synthetic versatility than the bidentate 2,2′-bipyridine and 1,10-phenanthroline ligands by virtue of possible variation of the bridging atom, the heterocyclic rings (e.g. 2-pyridyl, 2-methylimidazole, or 2-pyrrazolyl),[7] and the substituents on the heterocyclic rings. Such versatility might be expected to allow a subtle control over the redox chemistry which is not possible with bipyridine or phenanthroline species. Furthermore, electrochemical studies of the bis(ligand)cobalt complexes indicate the ability of these tripodal ligands to stabilize low oxidation states of metal centres to an extent comparable with 2,2′-bipyridine.[8] It was our hope that by subtle variation of the redox properties of the polypyridyl complexes of carbonylrhenium centres, a new mechanistic insight would be possible into the role of such metal species in their catalysis of $CO_2$ reduction processes.



$py_3X$ (X = N, CH, P)

The recent report by Juris *et al.*[9] of the synthesis of a related species containing the potentially tridentate ligand tpy, which was purported to be '[Re(tpy)$(CO)_2$Cl]', and of its ability to catalyse the electrochemical reduction of carbon dioxide, gave impetus to the proposal for the mechanistic studies of bis(carbonyl)rhenium species containing the tripodal ligands. However, during the synthetic aspects of this work, a number of anomalies arose relating to the characterization of these '[Re(tridentate)$(CO)_2$Cl]' complexes—in particular, the tendency of terpyridine to function as a bidentate rather than a tridentate ligand, and the ambidentate (bidentate/tridentate) ligating properties of the tripodal ligands.

The present paper reports structural and spectroscopic studies of carbonylrhenium compounds of these tripyridyl ligands, together with some initial observations on their electrochemistry and reactivity.

## EXPERIMENTAL

### Materials

[Re$(CO)_5$Cl] (Pressure Chemical Co.), 2,2′-bipyridine (Strem) and 2,2′:6′,2″-terpyridine (Aldrich) were used as supplied; all other chemicals and solvents were of AR grade (where available). For the electrochemical experiments, the solvent 1-methyl-2-pyrrolidinone (NMP; Aldrich HPLC grade) was purified by fractional distillation under reduced pressure following drying over anhydrous $MgSO_4$. *N*,*N*-Dimethylformamide (DMF; BDH) was twice fractionally distilled under vacuum. Acetonitrile (BDH HIPerSolv 'Far UV'), used for the conductance measurements, was dried over calcium hydride and fractionally distilled. Tetra-n-butylammonium tetrafluoroborate (TBA.$BF_4$; Fluka; puriss) was used as the supporting electrolyte.

### Instrumentation

Infrared spectra were measured in dichloromethane solution using a Perkin–Elmer 1600 Series FTIR. All electronic spectra were recorded on a Varian Cary 219 spectrophotometer. Electrochemical measurements were performed in an argon atmosphere and were recorded on a BAS 100A Electrochemical Analyzer using a glassy carbon working electrode and an $Ag^+/Ag$ reference electrode (0.01 M $AgNO_3$ in acetonitrile/0.1 M TBA.$BF_4$; which is +0.31 v vs s.s.c.e.). Conductance measurements in acetonitrile ($CH_3CN$) were performed with Kerr Universal B221 conductance bridge. Microanalyses were performed within the Department (JCUNQ) or by the Canadian Microanalytical Service (Delta, B.C.).

## Synthesis of ligands

Tris(2-pyridyl)amine,[10] tris(2-pyridyl)methane,[11] tris(2-pyridyl)methanol[12] and tris(2-pyridyl)phosphine[11] were prepared by literature methods.

## Synthesis of rhenium compounds

The synthesis of the rhenium complexes was from a general method described by Juris *et al.*[9]

### (2,2′-Bipyridine)tricarbonylchlororhenium(I), [Re(bpy)(CO)$_3$Cl]

2,2′-Bipyridine (72.5 mg, 0.46 mmol) was added to a solution of [Re(CO)$_5$Cl] (167.5 mg, 0.46 mmol) in toluene (80 ml, 80°C) under an argon atmosphere, which resulted in an immediate colour change from almost colourless to bright yellow and precipitation of a yellow complex within 1 min. The mixture was stirred and heated overnight. On cooling, the yellow precipitate was isolated by filtration, washed with petroleum spirit, and air-dried. Yield: 181 mg, 85%. The product was recrystallized twice from dichloromethane/petroleum spirit. Analysis: Calcd for $ReC_{13}H_8ClN_2O_3$: C, 33.8; H, 1.75; N, 6.1. Found: C, 33.7; H, 1.79; N, 6.1%.

### Tricarbonylchloro(2,2′:6′,2″-terpyridine)-rhenium(I) hydrate, [Re(tpy)(CO)$_3$Cl].H$_2$O

2,2′:6′,2″-Terpyridine (56.8 mg, 0.24 mmol) was added to a solution of [Re(CO)$_5$Cl] (88.1 g, 0.24 mmol) in toluene (30 ml, 60°C) under an argon atmosphere. The solution gradually deepened in colour with a yellow precipitate forming after *ca* 20 minutes. The mixture was stirred and maintained at 80°C overnight. On cooling, the yellow precipitate was collected by filtration and recrystallized from dichloromethane/petroleum spirit. Yield: 100 mg, 80%. Analysis: Calcd for $ReC_{18}H_{11}ClN_3O_3.H_2O$: C, 38.8; H, 2.35; N, 7.5; Cl, 6.4. Found: C, 38.7; H, 2.33; N, 7.5; Cl, 6.4%.

### Tricarbonylchloro{tris(2-pyridyl)amine}-rhenium(I) and Dicarbonylchloro-{tris(2-pyridyl)amine}rhenium(I), [Re(py$_3$N)(CO)$_x$Cl] ($x = 2,3$)

Tris(2-pyridyl)amine (162 mg, 0.65 mmol) was added to a solution of [Re(CO)$_5$Cl] (235 mg, 0.65 mmol) in toluene (110 ml, 82°C) under a nitrogen atmosphere. The mixture was heated and stirred while illuminated by a 100 W tungsten floodlight for 70 h. The resultant pale orange solution was separated from a red precipitate by centrifugation. The supernatant was evaporated (rotary evaporator) to yield a pale orange compound.

For the pale orange compound, [Re(py$_3$N)(CO)$_3$Cl]: yield = 202 mg, 56% (based on total conversion of [Re(CO)$_5$Cl] to this product). Analysis: Calcd for $ReC_{18}H_{12}ClN_4O_3$: C, 39.0; H, 2.37; N, 10.1. Found: C, 39.3; H, 2.30; N, 10.0%.

For the red compound, [Re(py$_3$N)(CO)$_2$Cl]: yield = 95 mg, 28% (based on total conversion of [Re(CO)$_5$Cl] to this product). Analysis: Calcd for $ReC_{17}H_{12}ClN_4O_2 \cdot 0.25C_6H_5CH_3$: C, 41.0; H, 2.57; N, 10.2; Cl, 6.5. Found: C, 40.6; H, 2.73; N, 9.6; Cl, 7.2%.

### Tricarbonylchloro{tris(2-pyridyl)phosphine}-rhenium(I), [Re(py$_3$P)(CO)$_3$Cl]

Tris(2-pyridyl)phosphine (131 mg, 0.49 mmol) was added to a solution of [Re(CO)$_5$Cl] (178 mg, 0.49 mmol) in toluene (80 ml, 70°C) under an argon atmosphere. The mixture was heated and stirred while illuminated by a 100 W tungsten floodlight for 60 h. The volume of the reaction mixture was reduced to *ca* 10 ml (rotary evaporator) and a brown–orange solid was precipitated by the addition of petroleum spirit. The collected precipitate was recrystallized twice from dichloromethane/petroleum spirit. Yield = 150 mg, 56%. Analysis: Calcd for $ReC_{18}H_{12}ClN_3PO_3$: C, 37.9; H, 2.12; N, 7.4. Found: C, 37.6; H, 2.32; N, 7.8%.

Using a similar synthetic method, a yellow–orange complex containing the ligand tris(2-pyridyl)methane (py$_3$CH) was synthesized in 85% yield (based on a product [Re(py$_3$CH)(CO)$_3$Cl]).

## Crystallography

Crystals of [Re(tpy)(CO)$_3$Cl)].H$_2$O and [Re(py$_3$N)(CO)$_3$Cl] were grown by layer diffusion of petroleum spirit into solutions of the respective compounds in dichloromethane. Intensity data for [Re(tpy)(CO)$_3$Cl].H$_2$O and [Re(py$_3$N)(CO)$_3$Cl] were measured at room temperature using the $\omega$:$2\theta$ scan technique on an Enraf–Nonius CAD4F diffractometer fitted with graphite monochromated MoK$\alpha$ radiation, $\lambda = 0.7107$ Å. No decomposition of either crystal occurred during its respective data collection. Data were corrected for Lorentz and polarization effects and an analytical absorption was applied in each case.[13] Crystal data are given in Table 1.

**Table 1** Crystal data for *fac*-[Re(tpy)(CO)$_3$Cl].H$_2$O and *fac*-[Re(py$_3$N)(CO)$_3$Cl]

| Compound | [Re(tpy)(CO)$_3$Cl].H$_2$O | [Re(py$_3$N)(CO)$_3$Cl] |
|---|---|---|
| Formula | $C_{18}H_{13}ClN_3O_4Re$ | $C_{18}H_{12}ClN_4O_3Re$ |
| Mol. wt | 557.0 | 541.9 |
| Crystal system | Monoclinic | Triclinic |
| Space group | $P2_1/n$ | $P\bar{1}$ |
| $a$, Å | 7.432(3) | 13.761(2) |
| $b$, Å | 17.016(4) | 14.636(6) |
| $c$, Å | 14.466(2) | 11.110(2) |
| $\alpha$, deg | 90 | 110.70(2) |
| $\beta$, deg | 93.51(2) | 102.45(2) |
| $\gamma$, deg | 90 | 107.48(2) |
| $V$, Å$^{-3}$ | 1826.0 | 1862.2 |
| $Z$ | 4 | 4 |
| $D_c$(g cm$^{-3}$) | 2.026 | 1.933 |
| $F(000)$ | 1064 | 1056 |
| $\mu$, cm$^{-1}$ | 68.81 | 67.45 |
| Transmission factors (maximum) | 0.560; 0.401 | 0.747; 0.584 |
| $\Theta$ limits, deg | 1.5–25.0 | 1.5–24.0 |
| No. of data collected | 4165 | 5974 |
| No. of unique data | 3215 | 5842 |
| No. of unique reflections used with $I \geq 2.5\sigma(I)$ | 2435 | 3459 |
| $R$ | 0.028 | 0.038 |
| $g$ | 0.002 | 0.003 |
| $R_w$ | 0.029 | 0.039 |
| Residual $\rho_{max}$, e Å$^{-3}$ | 0.98 | 1.85 |

The structure of *fac*-[Re(tpy)(CO)$_3$Cl].H$_2$O was solved from the interpretation of the Patterson synthesis whilst that of *fac*-[Re(py$_3$N)(CO)$_3$Cl] was solved by direct methods. The structures were each refined by a full-matrix least-squares procedure based on $F$.[13] All non-H atoms were refined with anisotropic thermal parameters in [Re(tpy)(CO)$_3$Cl].H$_2$O and the Re, Cl, carbonyl groups and amine-N atoms in [Re(py$_3$N)(CO)$_3$Cl] were refined anisotropically; the remaining non-H atoms were refined with isotropic thermal parameters for the latter structure. Hydrogen atoms were included at their calculated positions. The locations of the py-N atom in the non-coordinating pyridyl rings were confirmed by comparing the associated bond distances for both conformations. The refinements were continued until convergence after the introduction of a weighting scheme of the form $w = [\sigma^2(F) + g|F|^2]^{-1}$. Refinement details are listed in Table 1.

Fractional atomic coordinates are given in Tables 2 and 3 and the numbering schemes for both compounds are shown in Figs 2 and 3 (diagrams drawn with ORTEP[14] at 25% and 15% probability ellipsoids, respectively). Scattering factors for neutral Re (corrected for $f'$ and $f''$) were from Ref. 15 and those for the remaining atoms were as incorporated in SHELX.[13] Calculations were performed on a SUN4/280 computer.

For both structures, full listings of the thermal parameters, hydrogen atom parameters, all bond distances and angles, and the observed and calculated structure factors are available on request from one of the authors (ERTT).

## RESULTS AND DISCUSSION

### Characterization and structural details

**_fac_-[Re(bpy)(CO)$_3$Cl]**

The [Re(bpy)(CO)$_3$Cl] species, and other [Re(bpy)(CO)$_3$X] compounds, have been characterized to have the chloro ligand *cis* to both ligating N atoms of the 2,2′-bipyridine ligand, with the three carbonyl ligands occupying a *facial* disposition in the coordination octahedron. A number of structural determinations of compounds of this type confirm the stereochemistry—

**Table 2** Fractional atomic coordinates ($\times 10^5$ for Re; $\times 10^4$ for other atoms) for *fac*-[Re(tpy)(CO)$_3$Cl].H$_2$O

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Re | 20257(3) | 5091(1) | 24385(1) |
| Cl | 4420(2) | 1481(1) | 2892(1) |
| O(1) | 2296(9) | 910(3) | 381(3) |
| O(2) | −886(8) | −711(3) | 1942(4) |
| O(3) | 4886(9) | −713(3) | 2073(5) |
| N(1) | 2027(7) | 305(3) | 3920(4) |
| N(2) | 228(6) | 1421(3) | 2952(3) |
| N(3) | −312(9) | 2388(3) | 908(4) |
| C(1) | 2164(10) | 791(4) | 1148(5) |
| C(2) | 200(10) | −247(4) | 2134(5) |
| C(3) | 3802(10) | −263(4) | 2201(5) |
| C(4) | 2833(9) | −303(4) | 4351(5) |
| C(5) | 3017(10) | −346(5) | 5306(5) |
| C(6) | 2378(11) | 254(6) | 5826(5) |
| C(7) | 1525(10) | 876(5) | 5392(5) |
| C(8) | 1345(9) | 899(4) | 4426(4) |
| C(9) | 334(8) | 1513(4) | 3890(4) |
| C(10) | −486(10) | 2137(4) | 4328(5) |
| C(11) | −1422(10) | 2684(4) | 3787(5) |
| C(12) | −1581(10) | 2596(4) | 2837(5) |
| C(13) | −744(9) | 1952(3) | 2450(5) |
| C(14) | −1067(9) | 1842(4) | 1423(4) |
| C(15) | −2182(10) | 1261(4) | 1066(5) |
| C(16) | −2498(12) | 1217(5) | 117(6) |
| C(17) | −1733(11) | 1749(5) | −430(5) |
| C(18) | −655(13) | 2316(5) | −17(5) |
| O(w) | 3298(10) | 2976(4) | 1554(5) |

**Table 3** Fractional atomic coordinates ($\times 10^5$ for Re; $\times 10^4$ for other atoms) for *fac*-[Re(py$_3$N)(CO)$_3$Cl]

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Re(1a) | 34973(4) | 67200(3) | 27333(5) |
| Cl(1a) | 3623(3) | 7229(3) | 852(3) |
| O(1a) | 5297(9) | 8895(9) | 4879(12) |
| O(2a) | 1868(8) | 7704(8) | 3301(11) |
| O(3a) | 3390(9) | 6046(9) | 5022(10) |
| C(1a) | 4630(10) | 8078(11) | 4108(15) |
| C(2a) | 2478(11) | 7324(10) | 3090(14) |
| C(3a) | 3431(10) | 6276(11) | 4148(14) |
| C(4a) | 5548(9) | 6519(9) | 2146(11) |
| C(5a) | 6290(10) | 6090(10) | 1870(13) |
| C(6a) | 6049(10) | 5048(10) | 1596(13) |
| C(7a) | 5045(9) | 4425(10) | 1583(12) |
| C(8a) | 4344(8) | 4917(9) | 1900(11) |
| N(1a) | 4599(7) | 5952(7) | 2180(9) |
| C(10a) | 2374(9) | 4252(9) | 908(11) |
| C(11a) | 1647(10) | 3272(10) | −165(13) |
| C(12a) | 762(11) | 3198(11) | −1108(14) |
| C(13a) | 652(10) | 4136(10) | −955(13) |
| C(14a) | 1430(10) | 5104(10) | 83(12) |
| N(2a) | 2282(7) | 5180(7) | 1040(9) |
| C(15a) | 3138(9) | 3803(9) | 2680(12) |
| C(16a) | 3984(12) | 3723(12) | 3494(15) |
| C(17a) | 3712(12) | 3209(12) | 4327(15) |
| C(18a) | 2636(12) | 2826(12) | 4267(16) |
| C(19a) | 1860(13) | 2922(12) | 3399(15) |
| N(3a) | 2113(9) | 3431(9) | 2616(12) |
| N(4a) | 3303(7) | 4340(8) | 1858(10) |
| Re(1b) | 80899(3) | 01144(3) | 26242(5) |
| Cl(1b) | 6763(2) | 8304(2) | 824(3) |
| O(1b) | 7629(9) | 9554(10) | 4898(11) |
| O(2b) | 9940(8) | 9400(8) | 3112(10) |
| O(3b) | 9734(9) | 12349(8) | 4791(11) |
| C(1b) | 7815(11) | 9810(11) | 4068(14) |
| C(2b) | 9231(10) | 9675(9) | 2893(13) |
| C(3b) | 9101(11) | 11518(11) | 3963(14) |
| C(4b) | 5773(9) | 10055(9) | 2303(12) |
| C(5b) | 4885(10) | 10318(11) | 2064(13) |
| C(6b) | 4932(11) | 11067(11) | 1595(13) |
| C(7b) | 5876(9) | 11601(10) | 1443(12) |
| C(8b) | 6765(9) | 11324(9) | 1772(11) |
| N(1b) | 6722(7) | 10564(7) | 2200(10) |
| C(10b) | 8041(9) | 11155(9) | 606(12) |
| C(11b) | 8092(9) | 11312(9) | −536(12) |
| C(12b) | 8340(10) | 10664(10) | −1510(13) |
| C(13b) | 8569(11) | 9822(11) | −1283(14) |
| C(14b) | 8501(9) | 9720(10) | −134(12) |
| N(2b) | 8244(7) | 10367(7) | 827(9) |
| C(15b) | 8363(9) | 12926(9) | 2241(12) |
| C(16b) | 8020(11) | 13638(10) | 2991(13) |
| C(17b) | 8691(12) | 14715(12) | 3572(16) |
| C(18b) | 9681(13) | 15058(13) | 3458(16) |
| C(19b) | 9998(12) | 14320(12) | 2709(15) |
| N(3b) | 9318(9) | 13240(9) | 2079(12) |
| N(4b) | 7755(8) | 11815(7) | 1600(10) |

for example, of [Re(bpy)(CO)$_3$(PO$_2$F$_2$)],[16] [Re(bpy)(CO)$_3$(HCOO)],[17] [Re(bpy)(CO)$_3$(NCBH$_3$)],[17] and a related dimeric hydrido species [Re$_2$(bpy)$_2$(CO)$_6$($\mu$-H)]Cl.[17]

The electrochemical characteristics, as well as the electronic and infrared spectral properties of this compound, are listed in Table 4, together with the data for the other compounds involved in this study. The infrared spectrum in the region 2100–1800 cm$^{-1}$ (carbonyl stretch) is shown in Fig. 1A, where three $\nu$(CO) absorptions are observed (point group symmetry $C_s$).

### *fac*-[Re(tpy)(CO)$_3$Cl]

The physical properties of the compound assigned as [Re(tpy)(CO)$_2$Cl] by Juris *et al.*[9] are virtually identical to those of [Re(bpy)(CO)$_3$Cl] (Table 4). This led us to consider an alternative formulation in which the tpy ligand was bidentate and the structure analogous to [Re(bpy)(CO)$_3$Cl]: certainly, the infrared characteristics (viz. the *three* $\nu$(CO) absorptions, Fig. 1B) and the conductance (indicating a zero-charged species) favoured the formulation [Re(tpy)(CO)$_3$Cl]. A similar rationalization has been made previously for the related compound [Re(tpy)(CO)$_3$(NO$_3$)].[18]

Accordingly, we undertook an X-ray crystal structure determination of the terpyridine compound to settle this ambiguity.

The molecular structure of *fac*-[Re(tpy)-$(CO)_3Cl].H_2O$ is shown in Fig. 2 and selected bond distances and angles are given in Table 5. The Re atom exists in a distorted octahedral environment defined by a *facial* arrangement of the three carbonyl groups, and a Cl atom and two N atoms which occupy the other octahedral face. The N atoms are *cis* and are derived from the tpy ligand which is functioning in the bidentate mode. The non-coordinating N atom, N(3), is directed away from the Re atom and the Re · · · N separation is 4.20 Å. The major distortion from regular octahedral symmetry arises as a result of the restricted bite angle of the chelate; N(1)–Re–N(2) 75.2(2)°. The N(1)–C(8)C(9)–N(2) torsion angle is −1.1° and the N(2)–C(13)C(14)–N(3) torsion angle is −114.9°. $[Re(tpy)(CO)_3Cl].H_2O$ was found to crystallize as a monohydrate and this water molecule is closely associated with the Cl and N(3) atoms. The Cl · · · O(w) and N(3) · · · O(w) separations are calculated to be 3.27 and 2.96 Å, respectively.

### $[Re(py_3N)(CO)_xCl]$ ($x = 2, 3$)

Using a synthetic procedure analogous to that for *fac*-$[Re(bpy)(CO)_3Cl]$ and *fac*-$[Re(tpy)(CO)_3Cl]$, a product was isolated which exhibited similar infrared spectral characteristics when $[Re(CO)_5Cl]$ was reacted with $py_3N$.

When the synthesis was repeated but under intense irradiation by visible light, two products were formed. A toluene-soluble form, which was identical to product obtained in the absence of light, has the infrared spectrum shown in Fig. 1C, and an X-ray structural determination indicates that the tripodal ligand is coordinated in a bidentate manner and the formulation of the complex is *fac*-$[Re(py_3N)(CO)_3Cl]$.

The molecular structure of *fac*-$[Re(py_3N)$-$(CO)_3Cl]$ is shown in Fig. 3, and selected interatomic parameters are given in Table 6. There are two molecules in the crystallographic asymmetric unit for this compound, designated **a** and **b** respectively. The numbering scheme for molecule **a** is shown in Fig. 3 and that of molecule **b** is identical. There are no major differences between molecules **a** and **b** of $[Re(py_3N)(CO)_3Cl]$, with the maximum difference occurring for the N(1)–Re–C(3) angle of 92.1(4)° for molecule **a** compared with 94.7(5)° for molecule **b**. As found for the tpy derivative, the Re atom in $[Re(py_3N)(CO)_3Cl]$ exists in a distorted octahedral environment with a *facial* arrangement of the three carbonyl groups. The remaining three positions are occupied by the Cl atom and two N atoms of the potentially tridentate $py_3N$ ligand. The amine N atom, N(4), is 3.18 Å (3.19 Å for molecule **b**) from the central Re atom, which does not indicate a significant bonding interaction between these atoms. The N(1)–Re–N(2) chelate angle is 80.8(3)° {81.8(3)° for molecule **b**} which represents the maximum deviation from ideal octahedral symmetry in the structure. The N–Re–N chelate angles are larger here than in the $[Re(tpy)(CO)_3Cl]$ structure {75.2(2)°} which reflects the reduced steric strain in the six-membered $\overline{N(1)C(8)N(4)C(10)N(2)Re}$ ring in $[Re(py_3N)(CO)_3Cl]$ compared with the five-membered $\overline{N(1)C(8)C(9)N(2)Re}$ ring formed in $[Re(tpy)(CO)_3Cl]$.

The toluene-insoluble compound isolated from

Table 4 Spectral and electrochemical data

| Compound | Electrochemistry[a] $E_{p,c}$ | Electrochemistry[a] $E_{p,a}$ | Electronic spectra[c] $\lambda_{max}$ (nm) | Infrared spectra[d] $\nu$(CO) ($cm^{-1}$) |
|---|---|---|---|---|
| $[Re(bpy)(CO)_3Cl]$ | −1.71 | −1.62 | 370, 291, 233 | 2022, 1916, 1899 |
| $[Re(tpy)(CO)_3Cl]$ | −1.71 | −1.64 | 374, 305, 255 sh | 2022, 1918, 1897 |
| $[Re(py_3N)(CO)_3Cl]$ | −2.27[b] | | 300, 258, 226 sh | 2023, 1916, 1897 |
| $[Re(py_3N)(CO)_2Cl]$ | −2.34[b] | | 450, 342, 255 | 1900, 1824 |
| $[Re(py_3P)(CO)_3Cl]$ | | | | 2023, 1932, 1897 |
| $[Re(py_3CH)(CO)_2Cl]$ | | | | 1896, 1819 |

[a] Cyclic voltammetry measurements at glassy carbon working electrode, relative to $Ag/Ag^+$ reference electrode; solvent NMP/0.1M $TBA.BF_4$, except for $[Re(tpy)(CO)_3Cl]$ (DMF/0.1M $TBA.BF_4$). Scan rate 100 mV $s^{-1}$. [b] Irreversible. [c] Acetonitrile solution. [d] Dichloromethane solution, except for $[Re(py_3P)(CO)_3Cl]$ (nujol mull), and $[Re(py_3CH)(CO)_2Cl]$ (acetonitrile solution).

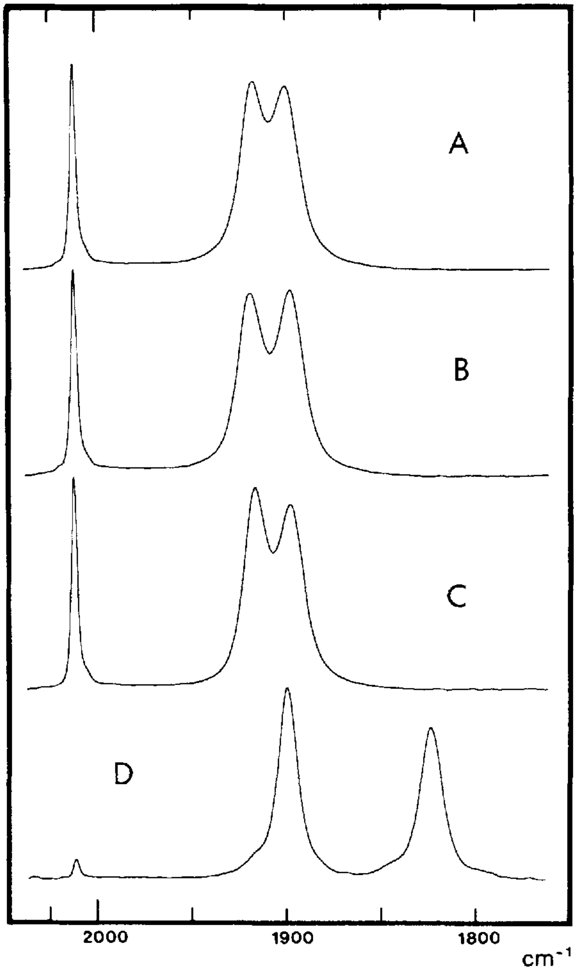


**Figure 1** Infrared spectra (carbonyl stretch region) in dichloromethane solution for selected compounds: A, *fac*-$[Re(bpy)(CO)_3Cl]$; B, *fac*-$[Re(tpy)(CO)_3Cl]$; C, *fac*-$[Re(py_3N)(CO)_3Cl]$; D, $[Re(py_3N)(CO)_2Cl]$.

this synthesis exhibits only two $\nu$(CO) absorption peaks (Fig. 1D; Table 4), consistent with either $[Re(py_3N)(CO)_2Cl]$ ($C_s$) or the symmetrical $[Re(py_3N)(CO)_3]Cl$ ($C_{3v}$) formulations. However, conductance measurements indicate a zero-charged species. Although we have not yet been successful in growing satisfactory crystals of this compound for a structural determination, we are confident that this species is $[Re(py_3N)(CO)_2Cl]$, where the $py_3N$ ligand is now tridentate.

Accordingly, the ligand $py_3N$ exhibits ambidentate behaviour with respect to its coordination with the carbonylrhenium(I) centres.

**$[Re(py_3CH)(CO)_xCl]$ and $[Re(py_3P)(CO)_3Cl]$**

Synthesis of the carbonylrhenium(I) compounds containing the tripodal ligands $py_3CH$ and $py_3P$ were carried out using the same general technique as for the $py_3N$ analogue.

In the case of $py_3P$, only one product could be detected, and it exhibited three $\nu$(CO) absorpotions in the infrared spectrum (Table 4). By analogy with the *fac*-$[Re(bpy)(CO)_3Cl]$, *fac*-$[Re(tpy)(CO)_3Cl]$ and *fac*-$[Re(py_3N)(CO)_3Cl]$ compounds, it may confidently be formulated as *fac*-$[Re(py_3N)(CO)_3Cl]$, with the ligand $py_3P$ being bidentate.

For $py_3CH$, a product was isolated with a complicated infrared spectrum in the $\nu$(CO) region. By analogy with the $[Re(py_3N)(CO)_xCl]$, the spectrum is consistent the isolated product being a mixture of *fac*-$[Re(py_3CH)(CO)_3Cl]$ and $[Re(py_3CH)(CO)_2Cl]$ in which the $py_3CH$ ligand has coordinated both as a bidentate and tridentate ligand. Indeed, in a preliminary separation experiment utilizing the differing solubilities of the two components in dichloromethane, the less soluble yellow compound exhibited an IR spectrum analogous to that of $[Re(py_3N)(CO)_2Cl]$ (Table 4); the remaining component, although slightly contaminated with the yellow less soluble species, exhibited an IR spectrum consistent with that of *fac*-$[Re(py_3N)(CO)_3Cl]$.

It should be noted that examples are known in which $py_3CH$ exhibits bidentate and tridentate

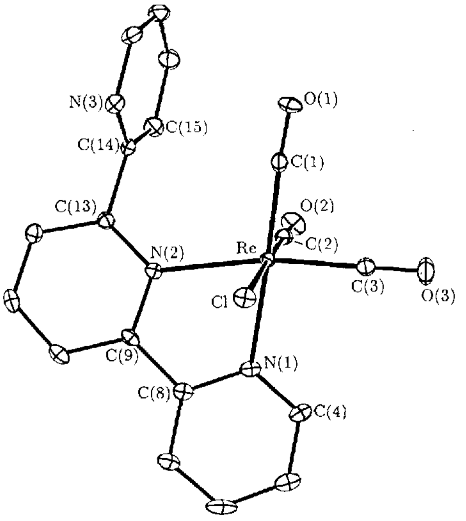


**Figure 2** Molecular structure and numbering scheme for *fac*-$[Re(tpy)(CO)_3Cl].H_2O$. Atoms otherwise not indicated are carbons. Hydrogen atoms have been omitted for clarity.

**Table 5** Selected bond distances (Å) and angles (deg) for *fac*-[Re(tpy)(CO)$_3$Cl].H$_2$O

| Atoms | Distance | Atoms | Distance |
|---|---|---|---|
| Re-Cl | 2.488(2) | Re-N(1) | 2.170(5) |
| Re-N(2) | 2.206(5) | Re-C(1) | 1.936(7) |
| Re-C(2) | 1.901(7) | Re-C(3) | 1.908(7) |
| N(1)-C(4) | 1.331(8) | N(1)-C(8) | 1.365(9) |
| C(8)-C(9) | 1.477(9) | N(2)-C(9) | 1.362(7) |
| N(2)-C(13) | 1.342(8) | C(13)-C(14) | 1.501(9) |
| N(3)-C(14) | 1.335(8) | N(3)-C(18) | 1.35(1) |
| **Atoms** | **Angle** | **Atoms** | **Angle** |
| Cl-Re-N(1) | 83.6(1) | Cl-Re-N(2) | 83.2(1) |
| Cl-Re-C(1) | 90.6(2) | Cl-Re-C(2) | 178.0(2) |
| Cl-Re-C(3) | 90.8(2) | N(1)-Re-N(2) | 75.2(2) |
| N(1)-Re-C(1) | 174.0(2) | N(1)-Re-C(2) | 94.4(2) |
| N(1)-Re-C(3) | 96.3(3) | N(2)-Re-C(1) | 102.7(2) |
| N(2)-Re-C(2) | 96.6(3) | N(2)-Re-C(3) | 170.0(2) |
| C(1)-Re-C(2) | 91.4(3) | C(1)-Re-C(3) | 85.4(3) |
| C(2)-Re-C(3) | 89.1(3) | Re-C(1)-O(1) | 175.4(6) |
| Re-C(2)-O(2) | 178.9(6) | Re-C(3)-O(3) | 178.4(6) |
| Re-N(1)-C(4) | 124.1(5) | Re-N(1)-C(8) | 115.7(4) |
| N(1)-C(8)-C(9) | 115.8(5) | C(8)-C(9)-N(2) | 116.0(5) |
| Re-N(2)-C(9) | 114.6(4) | Re-N(2)-C(13) | 127.5(4) |
| N(2)-C(13)-C(14) | 120.0(5) | C(13)-C(14)-N(3) | 114.7(6) |

coordination behaviour in the complexes [AuMe$_2$(py$_3$CH)]$^{+7}$ and [Ru(py$_3$CH)$_2$]$^{2+}$,[11] respectively.

## Comments on the synthetic method

The synthetic results are consistent with reported photochemical characteristics of [Re(CO)$_5$Cl][19] and CO-substituted derivatives such as *fac*-[Re(bpy)(CO)$_3$Cl].[20] The electronic transition giving rise to absorption by [Re(CO)$_5$Cl] in the visible region (*ca* 366 nm) has been assigned mainly LF character, and photolysis in the absence of other ligands leads to the formation of

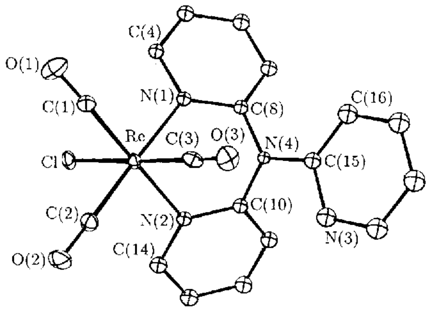


**Figure 3** Molecular structure and numbering scheme for *fac*-[Re(py$_3$N)(CO)$_3$Cl] (molecule **a**). Atoms otherwise not indicated are carbons. Hydrogen atoms have been omitted for clarity. The numbering scheme for molecule **b** is identical to that shown for molecule **a**.

**Table 6** Selected bond distances (Å) and angles (deg) for *fac*-[Re(py$_3$N)(CO)$_3$Cl]

| | Distances | |
|---|---|---|
| Atoms | Molecule **a** | Molecule **b** |
| Re-Cl | 2.477(3) | 2.476(3) |
| Re-N(1) | 2.208(8) | 2.186(9) |
| Re-N(2) | 2.191(9) | 2.197(9) |
| Re-C(1) | 1.92(1) | 1.89(1) |
| Re-C(2) | 1.91(1) | 1.87(1) |
| Re-C(3) | 1.91(1) | 1.90(1) |
| N(1)-C(4) | 1.34(1) | 1.35(1) |
| N(1)-C(8) | 1.35(1) | 1.35(1) |
| N(2)-C(10) | 1.36(1) | 1.35(1) |
| N(2)-C(14) | 1.35(1) | 1.35(1) |
| N(3)-C(15) | 1.33(2) | 1.33(2) |
| N(3)-C(19) | 1.37(2) | 1.38(2) |
| N(4)-C(8) | 1.41(1) | 1.43(1) |
| N(4)-C(10) | 1.41(1) | 1.40(1) |
| N(4)-C(15) | 1.41(1) | 1.40(1) |
| | **Angles** | |
| **Atoms** | **Molecule a** | **Molecule b** |
| Cl-Re-N(1) | 85.1(2) | 84.4(2) |
| Cl-Re-N(2) | 83.6(2) | 82.6(2) |
| Cl-Re-C(1) | 92.2(4) | 92.8(4) |
| Cl-Re-C(2) | 92.9(4) | 93.0(4) |
| Cl-Re-C(3) | 177.1(4) | 178.2(4) |
| N(1)-Re-N(2) | 80.8(3) | 81.8(3) |
| N(1)-Re-C(1) | 96.0(4) | 94.8(4) |
| N(1)-Re-C(2) | 176.2(4) | 177.0(4) |
| N(1)-Re-C(3) | 92.1(4) | 94.7(5) |
| N(2)-Re-C(1) | 174.9(4) | 174.5(5) |
| N(2)-Re-C(2) | 95.8(4) | 96.5(4) |
| N(2)-Re-C(3) | 95.2(5) | 95.7(4) |
| C(1)-Re-C(2) | 87.3(5) | 86.7(5) |
| C(1)-Re-C(3) | 88.8(6) | 88.8(6) |
| C(2)-Re-C(3) | 89.9(5) | 87.8(5) |
| Re-C(1)-O(1) | 177(1) | 176(1) |
| Re-C(2)-O(2) | 179(1) | 177(1) |
| Re-C(3)-O(3) | 177(1) | 178(1) |
| Re-N(1)-C(4) | 120.1(7) | 121.0(8) |
| Re-N(1)-C(8) | 121.1(7) | 122.3(7) |
| N(1)-C(8)-N(4) | 116.2(9) | 116.0(9) |
| Re-N(2)-C(10) | 120.4(7) | 121.6(8) |
| Re-N(2)-C(14) | 122.4(8) | 121.4(7) |
| N(2)-C(10)-N(4) | 117.1(9) | 117(1) |
| C(8)-N(4)-C(10) | 118.7(9) | 117.4(9) |
| C(8)-N(4)-C(15) | 123.2(9) | 122.8(9) |
| C(10)-N(4)-C(15) | 118.0(9) | 119.3(9) |
| N(4)-C(15)-N(3) | 113(1) | 115(1) |

the dimer, $[Re(CO)_4Cl]_2$.[19] In the presence of a ligand such as 2,2′-bipyridine, photolysis of $[Re(CO)_5Cl]$ results in the quantitative formation of $[Re(bpy)(CO)_3Cl]$,[19,20] and these photosubstitution processes are very much more rapid than thermal CO-substitution rates. On the other hand, the lowest energy absorption of *fac*-$[Re(bpy)(CO)_3Cl]$-type compounds is assigned principally to a $Re \rightarrow X(\pi^*)$ CT transition, in which the excited state is not substitutionally labilized.[20]

In the present instance, the thermal reactions of the potentially tridentate ligands tpy and $py_3N$ with $[Re(CO)_5Cl]$ give rise to the *fac*-[Re(ligand)$(CO)_3Cl$] species in which the tripyridyl ligands are bidentate, in a reaction which is analogous to that of the bidentate ligands bpy and phen with $[Re(CO)_5Cl]$. In the presence of light, the reaction involving the $py_3N$ or $py_3CH$ ligands also produces the tridentate species $[Re(py_3X)(CO)_2Cl]$ consistent with the CO-labilization of $[Re(CO)_5Cl]$ by visible light absorption. Additional observations reinforce this assertion. Firstly, two separate syntheses involving the $py_3CH$ ligand, with identical reaction times but differing in that irradiation was maintained for the duration of the reaction in one case, but for only the first 10 minutes of reaction in the other, both gave products which were mixtures of the two components: although the ratio of the components may have varied, it is clear that the CO-labilization occurs in the initial stages of the reaction and therefore involves the reactant $[Re(CO)_5Cl]$. Secondly, attempts to promote coordination of the third N-donor of the potentially tridentate ligands tpy or $py_3N$ in the compounds *fac*-[Re(ligand)$(CO)_3Cl$] under irradiation were totally unsuccessful.

It is interesting to note that under the conditions used in the syntheses, neither tpy or $py_3P$ appears to give the corresponding tridentate compound. The reason for these observations is probably steric in origin. In compounds containing coordinated tpy, it is well documented that the metal–central N distance is significantly contracted compared with the metal–outer N distances, and this is presumably due to steric constraints imposed by the tridentate tpy ligand.[21]

The ligand tpy has been shown to exhibit ambidentate coordination behaviour: Deacon *et al.*[22] have synthesized and structurally characterized the series of ruthenium(II) complexes *cis,cis*-$[Ru(Cl)_2(CO)_2(tpy)]$ (in which tpy is bidentate), and the related species *cis*,*cis*-$[Ru(Cl)_2(CO)_2(tpyH)]^+$ in which the free pyridyl-N atom is protonated, as well as the corresponding decarbonylated species *cis*- and *trans*-$[Ru(Cl)_2(CO)(tpy)]$ (in which tpy is tridentate).

$Py_3P$, with its increased 'bite' angle compared with $py_3CH$ and $py_3N$, also appears to prefer bidentate coordination in the present case: it is noted that in structural studies of the $[Ru(py_3X)_2]^{2+}$ complexes,[11] the cations show increasing distortion from the ideal $D_{3d}$ symmetry with an increase in the bridgehead X–C(py) bond distance in the series $py_3N < py_3CH < py_3P$. As a further example, in the series of complexes $[Ru(py_3X)(NH_3)_3]^{2+}$ (X = N, CH, COH, P), only in the case of $py_3P$ did a tridentate species not form.[23]

## Nature of metal–ligand interaction for tripodal ligands $py_3X$

The title tripodal ligands are known to exhibit $\pi$-back-bonding interactions with low oxidation state metals.[8] Because of the presence of the bridging atom between the pyridyl rings the back-bonding characteristics of the tripodal ligands $py_3X$ (X = N, CH, P), relative to ligands such as bpy or phen which possess the $\alpha,\alpha'$-di-imine chromophore, are somewhat counter-intuitive. It has been suggested that the particular stereochemical requirements of these ligands may serve to maximize the appropriate metal–ligand interaction,[8] and molecular-orbital calculations are in progress to probe the nature of the bonding.[24]

The ambidentate nature of the coordination of $py_3N$ might therefore have been expected to provide additional insight into this issue, since in the bidentate coordination mode the chromophore is equivalent to two pyridyl rings separated by the bridging atom, in contrast with the tridentate coordination mode where the bridgehead atom may serve to constrain the three pyridyl rings in a conformation particularly favourable for overlap between the ligand $p_\pi$ and metal $t_{2g}$ orbitals. However, the $\nu$(CO) absorptions in the infrared spectra of the series of compounds *fac*-$[Re(bpy)(CO)_3Cl]$, *fac*-$[Re(tpy)(CO)_3Cl]$, *fac*-$[Re(py_3N)(CO)_3Cl]$, and *fac*-$[Re(py_3P)(CO)_3Cl]$ are virtually identical in nature and position (Table 4; Fig. 1); it has been acknowledged for some time that in substituted metal carbonyl compounds of this type, the CO-stretching frequency shifts are not a reliable means of assessing the $\pi$-bonding abilities of ligands.[25] Neither are the electrochemical characteristics of the compounds in this study particularly revealing, because the reduction of the compounds containing the ligand $py_3N$ are irreversible, compared with the reversible redox behaviour exhibited by the bpy- and tpy-containing species (Table 4).

## Carbon dioxide reactivity

In earlier studies, Juris *et al.*[9] reported that the compound characterized as '$[Re(tpy)(CO)_2Cl]$' chemically catalysed the electrochemical reduction of carbon dioxide in a similar manner to *fac*-$[Re(bpy)(CO)_3Cl]$.[2,6] In view of the present reassessment of the formulation of the tpy-containing species as *fac*-$[Re(tpy)(CO)_3Cl]$, in which tpy is bidentate rather than tridentate, the similarity is not unexpected.

We have observed that the *fac*-$[Re(py_3X)(CO)_3Cl]$ and $[Re(py_3X)(CO)_2Cl]$ compounds do mediate in the electrochemical reduction of $CO_2$. However, the initial reductions of the $[Re(py_3N)(CO)_xCl]$ ($x = 2, 3$) species occur at considerably more negative potentials ($E_{p,c} = -2.34$ and $-2.27$ V vs $Ag/Ag^+$, respectively) than those of *fac*-$[Re(bpy)(CO)_3Cl]$ and *fac*-$[Re(tpy)(CO)_3Cl]$ ($E_{p,c} = -1.71$ V in both cases; Table 4). Given that for the $CO_2/CO_2^{\cdot -}$ couple in water $E^\circ = -1.90$ V (vs normal hydrogen electrode;[26] i.e. *ca* $-2.5$ V vs $Ag/Ag^+$), the compounds containing the tripodal ligands $py_3X$ do not appear to be particularly attractive candidates for electrocatalysis of $CO_2$ reduction.

## CONCLUSIONS

The present work has shown an apparent special stability of species of the general formula *fac*-$[Re(L—L)(CO)_3L]$ where L—L is a bidentate ligand, even in instances where L—L is potentially tridentate. If the synthetic procedure (CO-substitution of $[Re(CO)_5Cl]$) is undertaken under irradiation by visible light, for the ligands $py_3N$ and $py_3CH$ compounds of the general formula $[Re(L_3)(CO)_2Cl]$ containing the respective tridentate ligands are also obtained, whereas for tpy and $py_3P$ they are not. The reason for this difference may be stereochemical in nature.

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