Synthesis and characterization of 6,7 and 8-coordinate monomeric complexes of tungsten obtained from reaction of $[\text{W}(\text{CO})_3(\text{MeCN})_3]$ with pyridine-2-thiol (pySH) and PPh₃

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Complexes $[\text{W}(\text{CO})_3(\text{PPh}_3)_2]$ 1, $[\text{W}(\text{CO})_3(\text{pySH})(\text{PPh}_3)]$ 2, $[\text{W}(\text{CO})_3(\text{pyS})_2(\text{PPh}_3)]$ 3 and $[\text{W}(\text{pyS})_3]$ 4 have been obtained from the reaction of $[\text{W}(\text{CO})_3(\text{MeCN})_3]$ with pyridine-2-thiol (pySH) and PPh₃ in refluxing THF. 1 and 2 are normal 6-coordinate complexes but 3 and 4 are unusual 7 and 8-coordinate complexes, respectively. The complexes have been characterized by IR, 1H and 31P NMR, mass spectra and elemental analysis.

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Pyridine-2-thiol (pySH) and its deprotonated derivative pyridine-2-thiolato group (pyS⁻) are very interesting ligands because of their diversity of coordination modes with transition metals.⁹ The synthesis and structure of the 6-coordinate chromium complex $[\text{Cr}(\text{pyS})_3]$ in which the pyS⁻ group acts as a chelating ligand by coordination through both N and S atoms have been reported.⁶ Youmao Shi and co-workers¹⁰ reported that treatment of $[\text{Mo}(\text{CO})_3(\text{MeCN})_3]$ with pyridine-2-thiol and PPh₃ in THF solution at 50°C yields three interesting bridged molybdenum complexes $[\text{Mo}_2(\mu-\text{pyS})_2(\text{CO})_2(\text{PPh}_3)]_2$, $[\text{Mo}_2(\mu-\text{pyS})_2(\text{CO})_2(\text{PPh}_3)]_2$ and $[\text{Mo}_2(\mu-\text{pyS})_2(\mu-\text{pyS})_2(\text{CO})_6]$ in which the pyS⁻ group acts either as a two-centre or three-centre bridging ligand. Deeming et al.¹¹ observed that reaction of $[\text{W}(\text{CO})_3(\text{MeCN})_3]$ with pySH in acetonitrile at room temperature gives two tungsten complexes $[\text{W}(\text{pyS})_2(\text{CO})_3]$ and $[\text{W}(\text{pySH})(\text{CO})_2]$ where pyS⁻ and pySH act as chelating and monodentate ligands respectively. Chromium, molybdenum and tungsten are three transition metals of the same group (Gr VI) and they have similar electronic configurations but differ in their sizes. Since the chemical nature of the transition metals are dependent on their sizes, it is expected that tungsten, which is the largest of the three atoms, will behave in a different way in its reaction with pySH. A reaction of $[\text{W}(\text{CO})_3(\text{MeCN})_3]$ has been carried out in a similar method as described by Youmao Shi et al.¹⁰ for the molybdenum analogue. The results are reported in this note.

Experimental

Reactions and manipulations were carried out in an atmosphere of dry oxygen-free nitrogen by the Schlenk technique. Solvents were dried by standard methods and distilled before use. $[\text{W}(\text{CO})_3]$, pySH and PPh₃ were Aldrich reagent grade chemicals and used as obtained. IR spectra were recorded on a Shimadzu FT IR 8101 spectrophotometer in CH₂Cl₂ and ¹H and ³¹P NMR on a Bruker DPX 400 spectrometer in CD₂Cl₂. The mass spectra were recorded with a Varian MAT CH7 instrument.

Reaction of $[\text{W}(\text{CO})_3(\text{MeCN})_3]$ with pyridine-2-thiol and triphenylphosphine

A mixture of $[\text{W}(\text{CO})_3]$ (0.267 g, 0.76 mmol) and acetonitrile (10 mL) was refluxed under nitrogen for 7 h. After the removal of volatiles under low pressure, $[\text{W}(\text{CO})_3(\text{MeCN})_3]$ was obtained as a yellow solid. pySH (0.084 g, 0.76 mmol), PPh₃ (0.200 g, 0.76 mmol) and THF (20 mL) were added to the yellow solid which after stirring gave a red solution. The solution was refluxed for 3 h. After evaporation of the solvent under reduced pressure, the residue was redissolved in CH₂Cl₂ and separated by preparative TLC on silica (eluant:hexane/CH₂Cl₂ 3:1, v/v) which gave four bands. These were collected and recrystallized from CH₂Cl₂/hexane at 0°C which afforded four crystalline complexes. $[\text{W}(\text{CO})_3(\text{PPh}_3)]$ 1 as pale yellow crystals (0.062 g, 10%) [Found: C, 58.98; H, 4.11; Req'd. for C₃₀H₇₈O₁₃P₂W: C, 58.54; H, 3.66%]; $[\text{W}(\text{CO})_3(\text{pySH})(\text{PPh}_3)]$ 2 as orange crystals (0.045 g, 9%) [Found: C, 48.28; H, 3.02; N, 1.96; Req'd. for C₃₀H₇₆O₁₁N₂P₂W: C, 48.43; H, 2.99; N, 2.09%]; $[\text{W}(\text{CO})_3(\text{pyS})_2(\text{PPh}_3)]$ 3 as red crystals (0.033 g, 6%) [Found: C, 48.37; H, 4.12; N, 3.67; Req'd. for C₃₀H₇₆O₁₁N₂P₂W: C, 38.23; H, 2.41; N, 3.88%] and $[\text{W}(\text{pySH})_3]$ 4 as pale yellow crystals (0.071 g, 15%) [Found: C, 38.23; H, 2.41; N, 3.89%;]
Results and discussion

Treatment of \([\text{W(CO)}_6(\text{MeCN})_3]\) with pySH and PPh\(_3\) in refluxing THF and work-up as detailed in the experimental section affords two 6-coordinate complexes \([\text{W(CO)}_6(\text{PPh})_3]\) \(1\) and \([\text{W(CO)}_6(\text{pySH})(\text{PPh})_3]\) \(2\), one 7-coordinate complex \([\text{W(CO)}_7(\text{pyS})_2(\text{PPh})_3]\) \(3\) and one 8-coordinate complex \([\text{W(pyS)}_4]\) \(4\) whose structures based on their analytical and spectroscopic data are shown.

The complexes were characterized from their IR, \(^1\text{H}\) and \(^{31}\text{P}{\text{[H}}}\)NMR and mass spectra. The spectral data of \(1\) [IR: \(\nu(\text{CO})\) 1888 (s) cm\(^{-1}\); \(^1\text{H}\) NMR: \(\delta 7.51\) (m, Ph protons); \(^{31}\text{P}{\text{[H}}}\)NMR: \(\delta 28.8\) (s, \(^{31}\text{P}\); mass: \(m/z\) 820 (M\(^+\))] shows only one \(\nu(\text{CO})\) frequency in the IR and only one phosphorus signal in the \(^{31}\text{P}{\text{[H}}}\)NMR but no signal for pyridine ring protons in the \(^1\text{H}\) NMR is seen suggesting it to be the complex \(\text{trans-[W(CO)}_6(\text{PPh})_3]\) \(1\) with \(D_{4d}\) symmetry and the molecular ion peak in the mass spectrum is consistent with the formulation. This complex was earlier reported by Hieber & Peterhans\(^5\) only on the basis of its IR spectrum [\(\nu(\text{CO})\) 1894 cm\(^{-1}\)]. IR spectrum of \(2\) showed four \(\nu(\text{CO})\) bands [2013 (vs), 1905 (s), 1880 (br), 1848 (br) cm\(^{-1}\)] in the region of terminal CO frequencies and one band at 3320 (br) cm\(^{-1}\) characteristic of N-H stretching frequency. \(^1\text{H}\) NMR showed two multiplets centred at \(\delta 7.40\) and 7.49 due to phenyl protons of PPh\(_3\), three sharp signals [\(\delta 6.87\) (t, 1H, \(J_{\text{HH}} = 6.6\) Hz), 7.50 (d, 1H, \(J_{\text{HH}} = 8.7\) Hz), 7.49 (t, 1H, \(J_{\text{HH}} = 6.1\) Hz)] for C-H protons and a broad signal at \(\delta 11.69\) (1H) for N-H proton of pySH ligand. Another C-H proton signal is obscured inside Ph signals. The presence of the N-H signal in both IR and \(^1\text{H}\) NMR indicates that the pySH ligand is bonded to tungsten through the S atom. \(^{31}\text{P}{\text{[H}}}\)NMR clearly showed a singlet at \(\delta 21.6\) suggesting that only one PPh\(_3\) ligand is present in the complex. The mass spectrum of \(2\) [\(m/z\) 669 (M\(^+\)), 557 (M\(^+\)-CO), 446 (M\(^+\)-4CO-pySH), 184 (M\(^+\)-4CO-pySH-PPh\(_3\))] showed the molecular ion peak and other peaks from its important fragments. All these spectral evidences suggest that the structure of \(2\) is correct.

The infrared spectrum of complex \(3\) showed two \(\nu(\text{CO})\) absorption bands [1927 (s), 1832 (s) cm\(^{-1}\)] very similar to those of the analogous 7-coordinate tungsten complex \([\text{W(CO)}_7(\text{pyS})_2(\text{PMe}_2\text{Ph})]\) \(5\) [1937 (s), 1850 (s) cm\(^{-1}\)] suggesting that they have very similar distribution of the carbonyl ligands. \(^1\text{H}\) NMR showed a multiplet in the region \(\delta 7.2-7.4\) for the phenyl protons of PPh\(_3\) but peaks for the pyS\(^-\) ligand were not well resolved due to fluxional behaviour of 7-coordinate complexes at room temperature\(^1\).

For 7-coordinate complexes the pentagonal bipyramid, the capped octahedron and the capped trigonal prism structures are possible. Not only are the differences between them small, but real complexes often have structures that deviate somewhat from the idealized ones, and because of small differences in energy of the three types of structures, at room temperature in solution they often show fluxional behaviour. \(^{31}\text{P}{\text{[H}}}\)NMR showed a sharp peak at \(\delta 35.0\) indicating the presence of only one PPh\(_3\) group. The mass spectrum showed the molecular ion peak and other peaks for its important fragments [\(m/z\) 722 (M\(^+\)), 694 (M\(^+\)-CO), 666 (M\(^+\)-2CO)]. Thus the spectral data are consistent with the proposed structure for \(3\) which is also identical with the X-ray crystallographically determined structure of the related complex \(5\).

The most interesting of the four complexes obtained is \(4\) because it is a new addition to the rare 8-coordinate monomeric complexes of tungsten.\(^{11,14,15}\).
Each of the pyS\(^-\) groups in 4 acts as a chelating ligand making it 8-coordinate. IR did not show any absorption bands in the carbonyl region (1750-2200 cm\(^{-1}\)) and \(^{31}\)P\(^{1}{^1}\)H\(^{1}\)NMR did not give any signal for P atom indicating that neither CO nor PPh\(_3\) was present in this complex. \(^{1}\)H NMR in CD\(_2\)Cl\(_2\) showed four peaks of equal intensity [\(\delta\) 7.55 (d, \(J=6.0\) Hz, H\(^8\)), 7.50 (d, \(J=8.6\) Hz, H\(^8\)), 7.37 (t, \(J=8.6\) Hz, H\(^5\)), 6.75 (t, \(J=6.0\) Hz, H\(^3\))] indicating the presence of four different types of protons in the pyridine ring. Since only one set of pyridine proton signals was obtained, all four pyS\(^-\) ligands in 4 are equivalent. The mass spectrum showed the molecular ion peak at m/z 624 (60\%) with proper isotopic pattern for tungsten and other peaks relevant to the fragments of its decomposition [m/z 514 (M\(^+\)-pyS), 404 (M\(^+\)-2pyS), 294 (M\(^+\)-3pyS), 184 (M\(^+\)-4pyS), 111 (pySH\(^+\)), 78 (py\(^+\))] confirming the formulation 4 for the new complex. Since all four pyS\(^-\) groups act as chelating ligands 4 is an 8-coordinate monomeric complex which may have either a square antiprism or a dodecahedral structure, the real structure can only be determined by an X-ray crystallographic study because spectroscopic results are not sufficient to ensure the real structures of 8-coordinate complexes. Tungsten being a large size transition metal extension of coordination number beyond six is not unlikely and several 7- and 8-coordinate tungsten complexes have been reported in the literature.

It is interesting to note that although PPh\(_3\) is not a constituent of the complex [W(pyS\(_n\))\(_3\)], we failed to prepare this complex in another reaction using only [W(CO)\(_3\)(MeCN)\(_3\)] and pySH in refluxing THF. Youmao Shi \textit{et al.} also reported a similar experience that an attempt to prepare the complex [Mo\(_3\)(\(\mu\)-pyS)\(_2\)(\(\mu\)-pyS)\(_3\)(CO)\(_6\)] by the reaction of [Mo(CO)\(_3\)(MeCN)\(_3\)] with pySH was a failure although the complex could be prepared from the same reaction in presence of PPh\(_3\).

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**References**